Jose H. Zagal · Fethi Bedioui *Editors*

Electrochemistry of N4 Macrocyclic Metal Complexes

Volume 2: Biomimesis, Electroanalysis and Electrosynthesis of MN4 Metal Complexes

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Foreword

Society's mounting concern for the well-being of our environment has given increased impetus to the development of new, efficient, sustainable, and clean industrial processes and energy sources at reasonable cost. Electrochemistry has an important role to play in these developments. Exploring and understanding nature's mechanisms for catalytic reactions gives important indicators towards productive research areas. Such is the case with porphyrins and phthalocyanines, which are the subject of this monograph.

The purpose of this book is to present and discuss the latest advances in the understanding and applications MN4, or also so-called M-N4, macrocycles, with a focus on porphyrins and phthalocyanine complexes. Different areas of electrochemistry are examined and linked through the catalytic properties of synthetic and naturally occurring MN4 complexes. The breadth of the subject is reflected in the contents of the two multiauthor volumes, which include electrocatalysis, energy conversion, biomimetic design, electrochemical monitoring, and electrosynthesis. The editors are to be congratulated for assembling contributions on all these topics by recognized experts in their fields.

I am certain that this two-volume monograph will be valuable to researchers in leading to new ideas and synergies, highlighting state of the art, addressing challenges, and bridging the gap between different areas of research in MN4 macrocycles. It will aid in driving this important field forward.

Coimbra University, Portugal — Christopher Brett

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 spectrophotochemistry. 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 nanosized 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.

Jose H. Zagal
Fethi Bedioui

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Editors and Contributors

About the Editors

Jose H. Zagal is Full Professor at the University of Santiago de Chile. He received a degree in Chemistry from the University of Chile and a Ph.D. in Chemistry from Case Western Reserve University. He was postdoctoral fellow at Brookhaven National Laboratory. He was awarded the *Presidential Chair in Science*, The Dr. Alberto Zanlungo Prize is a Fellow of the *International Society of Electrochemistry* and Fellow of *The Electrochemical Society*. He has published over 200 papers, three books, seven book chapters, and three patents. He has served on the Editorial Boards of the following journals: *Journal of AppliedElectrochemistry* (1988–2010), *Journal of the Chilean Chemical Society* (1984–2007) *Electrocatalysis*, (2009–2015) and is presently a member of the Editorial Board of: *Journal of Solid State Electrochemistry(Springer),* of the *International Journal of Electrochemistry (Endawi), Electrochemistry Communications*, *Journal of the Serbian Chemical Society, Electrochemical Energy Technology* and *Chimica Nova.* He has contributed in several areas or electrochemistry including electrocatalysis, conductive polymers, electroanalysis, corrosion, electrochemistry of macrocyclic complexes and is better known for developing reactivity descriptors for the electrocatalytic activity of molecular catalysts.

Fethi Bedioui holds a degree in Chemical Engineering from the Ecole Nationale Supérieure de Chimie de Paris, Diplôme d'Etudes Approfondies de Chimie Analytique, and a Doctorate from the Université Pierre et Marie Curie in Paris. He was a postdoctoral fellow at the Ecole Nationale Supérieure de Chimie de Lille. At present he is a senior researcher in the CNRS in Paris (France) and works in the *Unité de Technologies Chimiques et Biologiques pour la Santé (Chimie ParisTech/PSL University/CNRS/INSERM/Université Paris Descartes)* on the development and implementation of advanced molecular materials for electrocatalysis and electrochemical sensing devices applied to biotechnological issues. In particular, he is actively working in the fields of electrochemical sensors for biological systems, multi-sensor arrayed platform for screening biological markers, porphyrins and phthalocyanines-based molecular materials for electroanalysis and electrocatalysis, microelectrochemical patterning of surfaces using scanning electrochemical microscopy and label-free electrochemical detection of microRNAs. He has published over 250 papers, including books and book chapters. He is currently Chair of the "Analytical Electrochemistry" division of the International Society of Electrochemistry.

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Supramolecular Hybrid Organic/Inorganic Nanomaterials Based on Metalloporphyrins and Phthalocyanines

Tiago Araujo Matias, Gianluca Camillo Azzellini, Lúcio Angnes and Koiti Araki

1 Introduction

Porphyrins and phthalocyanines are 18 π-electrons aromatic macrocycles exhibiting rich optical, photochemical, coordination, catalytic, and electrocatalytic properties. The basic porphine ring is formed by the cyclization of four pyrrole rings through methine (=CH–) bridges, whereas phthalocyanine ring has imine (=N–) bridges and a benzene ring fused to the 3,4-positions of the pyrrole rings. Both, porphyrins and phthalocyanines exhibit the pyrrole nitrogen atoms turned inward generating a square planar coordination site with four-fold axial symmetry capable to chelate ions of most elements [1, 2]. These strong equatorial bonds favor the delocalization of metal electronic density throughout the macrocycle π-system imparting large effects on the axial ligands activating them for catalytic and electrocatalytic processes. Concomitantly, the strong equatorial bonding weakens the axial bonds making these ligands more labile and enhancing the turnover number. The presence of more electronegative nitrogen atoms at *meso*-positions and the expanded π-aromatic system of phthalocyanines diminish the basicity of inner nitrogen atoms lone pairs, imparting distinct electronic, charge transfer, and redox properties to the metallated porphyrins and phthalocyanines [3].

Those basic structures can be modified by incorporating substituents to the ring periphery. Phthalocyanine can be substituted at the fused benzene ring carbon atoms whereas porphyrin presents two possibilities as shown in Fig. 1 (a) substitution at the *meso*- or (b) substitution at the beta-pyrrolic positions. The substituents can be tailored in order to impart additional specific physicochemical properties, fundamental for controlling the interactions and the behavior of those macrocycles derivatives as building blocks in supramolecular systems [2]. In fact, biological

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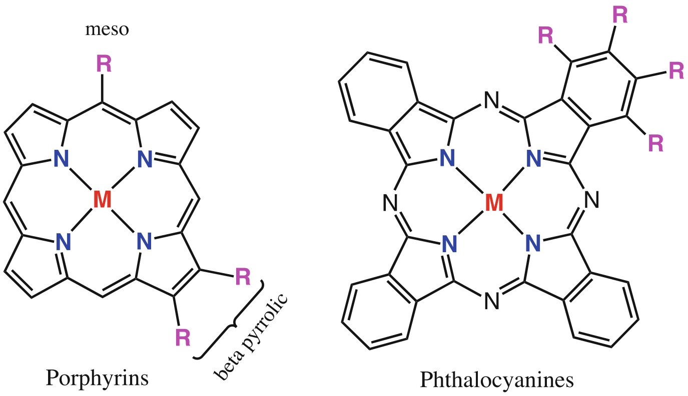


Porphyrins

Phthalocyanines

Fig. 1 Basic structures showing the square planar site available for coordination of a metal ion "M" and the ring substitution positions available in the porphyrins (*meso* and beta-pyrrolic) and phthalocyanine rings

systems are the best examples of how their structures should be engineered and organized in more complex systems in order to combine the static and dynamic properties of the parts synergically, generating functional molecular machines.

The extended π-system of porphyrins can be oxidized (in the 0.7–1.7 V range) and reduced (in the −0.8 to −1.8 V range) by up to two electrons, generating the respective radical cation and anion, which are followed by their dication and dianion. The redox potentials can be more or less shifted anodically or cathodically depending on the donor/acceptor characteristics of substituents, the axial ligands, the coordinated metal ion, and the microenvironment around the macrocycle ring. In fact, the central metal ion can introduce in addition to a bonding site, a redox and catalytic active site to the molecule. Some metal ions (for example Zn(II) and V=O) coordinate preferentially only one axial ligand generating complexes with square pyramidal geometry, but generally two axial ligands are present. In fact, the electrochemistry involving the coordinated transition metal ion is strongly dependent on the nature of the axial ligands. On the other hand, the induced electronic effects and the competition of solvent and coordinating molecules for the axial positions, the hydrophilic/hydrophobic character of the microenvironment around the site, and the steric and supramolecular interactions can influence their catalytic, electrocatalytic, and photoelectrochemical properties. The combination of porphyrins, expanded porphyrin, and phthalocyanines generating supramolecular homo and heterobinuclear systems and arrays, and multicomponent donor–acceptor conjugates with electroactive units (particularly fullerene and ferrocene) as model compounds for light-harvesting, have been recently reviewed by Torres et al. and will not be considered here [2].

In a previous review [4], we focused on the electrocatalytic properties of well-characterized supermolecules, generated by the coordination of transition metal complexes, such as ruthenium polypyridines and triangular ruthenium acetate clusters, to the pyridyl N-atoms of *meso*-pyridylporphyrins and pyridylporphyrazines. This approach was shown to be interesting for the development of supramolecular electrocatalysts since the peripheral transition metal complexes have strong enough electronic coupling with the macrocycle to influence its electronic, redox, and catalytic properties, particularly for multielectron redox processes. On the other hand, the electron-donating/withdrawing and oxidizing/reducing properties are strongly dependent on the oxidation state [5, 6]. Accordingly, the electrocatalytic properties can be tuned by controlling, electrochemically or using a molecular species added into the solution, the oxidation state of the peripheral complexes. This key aspects are further influenced by the degree of electronic coupling between the subunits, allowing them to respond more or less strongly to the redox state of ancillary groups. Thus, the presence of covalently bond redox relays is fundamental to impart to a supermolecular catalyst/photocatalyst the capacity of interacting and responding to the chemical potential of the environment and enhancing the stability and catalytic activity for multielectronic oxidation and reduction reactions.

Furthermore, the same peripheral complexes can act as redox sites increasing the electric conductivity by hopping mechanism, as well as additional interaction sites for formation of supramolecular systems by molecular recognition or by changing the structure of the activated complex centered on the metalloporphyrin. In short, peripheral metallation of porphyrins and porphyrazines can be used to generate supramolecular electrode materials particularly for application in electrochemical sensors and devices [6]. Molecular engineering also can improve the efficiency of photoinduced charge separation, the most fundamental process in photosynthesis, energy conversion, and photoelectrochemical devices.

In short, the principles of supramolecular chemistry can be explored to design new systems, particularly based on the combination of porphyrins and phthalocyanines with photochemically and electrochemically active donor/acceptor groups based on transition metal complexes and nanomaterials. Using this strategy it is possible to incorporate suitable metal clusters such as polyoxometalates as well as oxide and metal nanoparticles in a synergic way to develop supramolecular and hybrid materials with enhanced electrochemical/electrocatalytic and charge-transfer/charge separation properties. In this review, we will focus mainly on well-defined and well-characterized supramolecular systems constituted by porphyrins and peripheral electrochemically and photochemically active transition metal complexes, dendrimers made of porphyrins and phthalocyanines as well as nanostructured interfaces and hybrid nanomaterials obtained by binding metal and metal oxide nanocrystals, and carbon-based nanoparticles to those macrocycles.

2 Supramolecular Porphyrin Systems

Supramolecular systems can be rationalized as hierarchical systems where each stage is important on defining their properties, functionalities, and applications. In this context, transition metal complexes play major role as redox relays and active sites contributing to generate more complex new functionalities by the synergic interactions among the subunits [7].

The advancement in synthetic knowledge and methods in recent years are opening new possibilities for the preparation of hybrid nanomaterials encompassing metal and metal oxide nanocrystals, and carbon nanomaterials such as carbon nanotubes, fullerenes, and graphenes. However, generally the simple random mixture of components is not enough to get molecular and nanostructured materials with the desired properties. It is rather necessary to engineer them down to the molecular level to get the just right electronic coupling and molecular geometries, or the correct arrangement and connections at the interface to promote, for example, photoinduced dynamic processes for the conversion of light to electricity. For electrochemical and photoelectrochemical applications, it is fundamental that the supramolecular and hybrid materials be anchored on electrodes surface with appropriate orientation to maximize the kinetics and direct the processes to the desired direction.

2.1 Electrostatic Self-assembly

Self-assembly probably is one of the best expressions of intelligence at the molecular level. It is a property that depends entirely on the spatial organization of atoms creating large enough number of specific interactions to stabilize a unique molecular arrangement. Thus, those sites should be carefully planned considering the bridging groups as well as the active sites, chosen to assure the coupling of thermodynamically favorable processes. Some interesting examples of electrostatic assembly will be given below before going to covalently linked systems.

Tanaka et al. [8] proposed a very elegant strategy based on porphyrins peripherally modified with dibenzol[24]crown-8 and a secondary ammonium ion, able to form rotaxanes. In fact, the interaction of a porphyrin with a phthalocyanine lead to the formation of a stable π-stacked pseudo-rotaxane after end-capping the ammonium chains by reaction with Staudinger-phosphite in chloroform, followed by metallation with Cu(II). In acidic media, the ammine and phosphoramide groups are protonated generating a tetracationic species that can form ion-pairs with the tetraanionic $[\text{Cu-TSPP}]^{4-}$ species [9].

Positively and negatively charged species with extended delocalized π-systems such as porphyrins and phthalocianines are prone to electrostatic and π-stacking interactions forming supramolecular structures. Accordingly cationic protonated Fe(III) and Cu(II) *meso*-tetra(4-pyridyl)porphyrins and anionic $[H_4\text{-TSPP}]$ were explored to produce J-aggregates of those bis-porphyrins stabilized by Fe–O–Cu bonds [10]. Notice that the outward axial ligands can be rapidly exchanged by coordinating species present in solution characterizing interesting active sites for sensor application. In fact, that material can be used as Raman sensors of H_2O_2, NO_2^-, SO_3^{2-}, and N_3^- species, by monitoring changes in the sensitive bands at 661 (Cu–N out of plane bending) and 805 cm^{-1} (axial ligands) and exploring the enhanced sensitivity achieved by the synergic effects of those two metalloporphyrins connected by a μ-oxo bridge. That system was further explored generating nanotubes of $[\text{Fe-TPyP}]^{5+}$:$[\text{Cu-TPyP}]^{4+}$:$[\text{H}_4\text{-TSPP}]^{2-}$ porphyrins in 2:2:9 ratio.

2.2 *Coordinative Assembly*

The electrocalytic and photoelectrochemical properties of metalloporphyrins can be enhanced by the coordination of transition metal complexes such as ruthenium polypyridines ($[\text{Ru(bpy)}_2\text{Cl}]^+$ and $[\text{Ru(5-Clphen)Cl}]^+$), $[\mu\text{-ORu}_3(\text{OAC})_6(\text{py})_2]^+$ ruthenium acetate triangular clusters, $[\text{RuCl}_2(\text{CO})(\text{dmso})_2]$, $[\text{Ru(NH}_3)_5]^{2+}$, $[\text{Fe(CN)}_5]^{3-}$, $[\text{Rh(form)}_2(\text{TFA})_2]$, and $[\text{Ru(edta)}]^-$, as shown previously [4, 11, 12]. Their redox state can be electrochemically modified, or they can adjust by themselves to the electrochemical potential of the environment, inducing electronic donating and withdrawing effects (Fig. 2) stabilizing and activating the metalloporphyrin for multielectron redox reactions such as the tetraelectronic reduction of dioxygen to water and the oxidation of organic substrates coupled with oxygen atom transfer, respectively, mimicking the activity of cytochrome c oxidase [13–15] and cytochrome P450 [5, 16, 17]. On the other hand, photoelectrochemically active complexes, with suitable redox potentials in the ground and excited states, can exhibit intermolecular energy transfer processes enhancing the light-harvesting efficiency of dye-sensitized solar cells [18–20]. For example, the energy transfer direction could be inverted by coordination of imidazole to the axial positions of a tetraruthenated zinc porphyrin

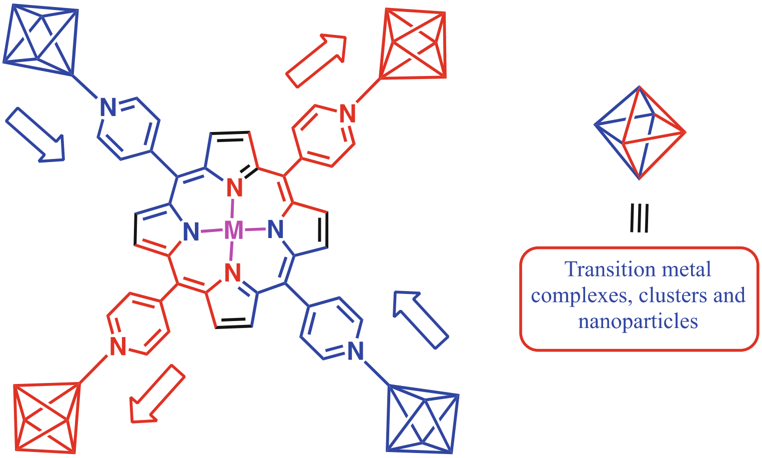
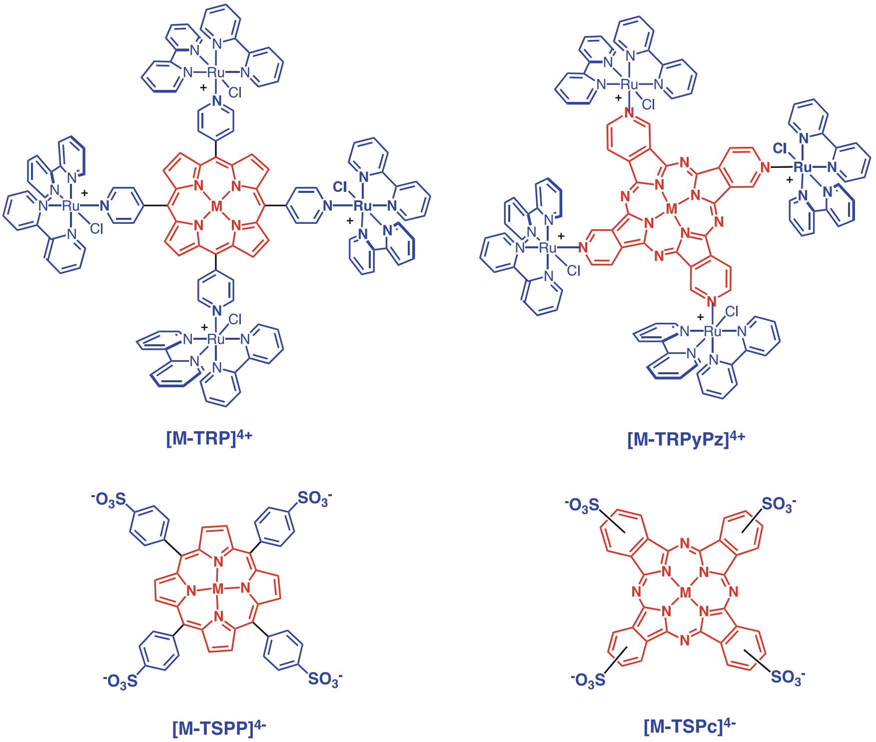


Fig. 2 Scheme showing the structure of a supramolecular species obtained by coordination of peripheral transition metal complexes, clusters or nanoparticles to the *N*-pyridyl atoms of *meso*-(tetrapyridyl)porphyrins, M-TPyPs, and exerting electron-withdrawing or donor effects that can be tuned by their oxidation state

with four [Ru(dm-2,2′-bpy)(bpy-P)]$^{2+}$ complexes bond to the four *meso*-positions [21]. Described in this section are the advancements achieved in the synthesis of new supramolecular systems by axial and peripheral coordination of transition metal complexes, and their spectroelectrochemical, electrocatalytic, and photoinduced electron transfer and photocatalytic properties.

The M-TPyPs substituted with [Ru(bpy)$_2$Cl]$^+$ form homogeneous and electrocatalytic active films by drop casting on electrodes surface. However, they are slowly solubilized even in the presence of an excess of a counteranion such as trifluoromethanesulfonate (TFMS) in the electrolyte solution. An interesting strategy to decrease the solubility improving the stability of tetrarutenated porphyrin films is by ion-pairing with [M-TSPP]$^{4-}$, a species exhibiting molecular recognition based on electrostatic and π–π interactions (Fig. 3) [22, 23]. Sulfur oxides (SO$_2$, SO$_3^{2-}$, and metabisulfites), commonly used as enzyme inhibitors and antioxidants for preserving many foodstuffs organoleptic properties, can produce disagreeable aroma and taste, as well as toxic effects when in high concentrations. Accordingly,



[M-TRP]$^{4+}$ [M-TRPyPz]$^{4+}$

[M-TSPP]$^{4-}$ [M-TSPc]$^{4-}$

Fig. 3 Structure of [M-TRP]$^{4+}$, [M-TRPyPz]$^{4+}$, [M-TSPP]$^{4-}$, and [M-TSPc]$^{4-}$ used for preparation of thin films by electrostatic assembly of a tetraruthenated porphyrin or porphyrazine with tetrasulfonated porphyrins or phthalocyanines glassy carbon electrodes modified with electrostatic-assembled $[ZnTRP]^{4+}$/$[FeTSPP]^{4-}$ ion-paired materials [24] were used as amperometric FIA-sensors of free sulfite present in fruit juices. An efficient FIA-cell was devised by combining a spiral-shaped gas diffusion cell and a wall-jet FIA amperometric cell in the same compact unit. This arrangement was free of interferences of all substances that do not form volatile species (glucose, sodium benzoate, pyrocatechol among others). Samples containing sulfite were injected in confluence with a sulfuric acid solution to convert it in SO_2 gas. This species in gaseous form permeates through a PTFE membrane and was collected by a carrier electrolyte solution, immediately before reaching the $[ZnTRP]^{4+}$/$[FeTSPP]^{4-}$-modified GC electrode surface. In this way, sulfite analyzes can be carried out with high reproducibility (SD = ±1.5 %), accuracy, and sensitivity (LOD = 0.043 ppm) in less than a minute, demonstrating its superior peformance when compared with the standard Monier-Williams method.

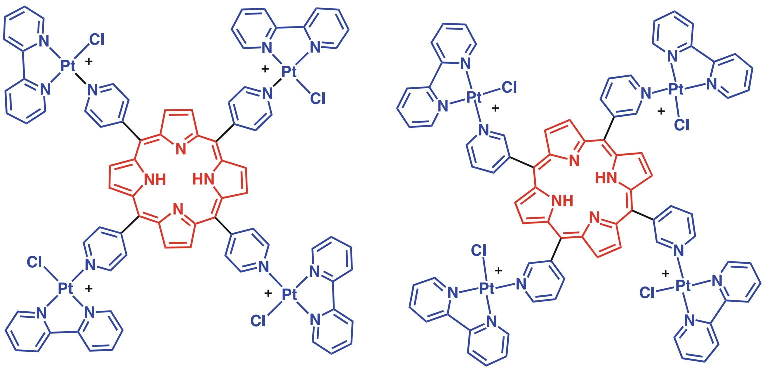
A tetraruthenated cooper(II) tetra(3,4-pyridyl)porphyrazine $[CuTRPyPz]^{4+}$ was prepared and used to generate ion-paired $[CuTRPyPz]^{4+}$/$[CuTSPP]^{4-}$ materials (Fig. 3) [25], which were characterized by spectroscopic and electrochemical methods. The electronic coupling in this system is much higher than in *meso*-tetra (pyridyl)porphyrin analogs because the pyridyl N-atoms are incorporated in the porphyrazine extended π-system, thus granting superior electronic interactions with peripheral ruthenium complexes. Functional materials were obtained as thin films by electrostatic assembly of tetracationic and tetraanionic species. The conduction and electrocatalytic properties were investigated by impedance spectroscopy and rotating disk voltammetry. The ion-paired material exhibited essentially metallic behavior near the Ru(III/II) redox potential as well as enhanced catalytic activity for oxidation of nitrite and sulfite in aqueous media.

Polymerization is another strategy to improve the stability of electrode materials. Accordingly, a new electropolymerizable tetraruthenated porphyrin was prepared by Isaacs et al. [26] by coordinating four $[Ru(5\text{-}NO_2phen)_2Cl]^+$ moieties to Ni-TPyP, in analogy to previously reported $[Ru(5\text{-}Clphen)_2Cl]^+$ derivative [27, 28]. *Meso*-tetra(4-pyridyl)porphyrin was refluxed with $[Ru(5\text{-}NO_2phen)_2(ACN)Cl]PF_6 \cdot 2H_2O$ in trifluoroethanol for 18 h, purified by alumina column chromatography, and characterized by ^{1}H-NMR, UV–Vis spectroscopy and electrochemistry. The cyclic voltammograms in DMF solution exhibited the typical Ru(III/II) process at 1.00 V versus Ag/AgCl, and two additional redox processes assigned to the formation of the radical anion and dianion species, respectively, were found at −0.64 and −0.90 V, whereas the reduction of $5\text{-}NO_2phen$ occurred at potentials below −1.0 V. The authors found a reversible wave at −0.70 V for the $[Ru(5\text{-}NO_2phen)_2Cl_2]$ complex in DMF, assigned to a redox process involving the nitro group. Interestingly, this same process become irreversible in the tetraruthenated porphyrin leading to the formation of hydroxylamine radicals whose oxidation to the respective radical cation was responsible for the electropolymerization and deposition of an electrochemically active material at the high scan rate of 0.5 V/s. However, no current enhancement of the voltammetric waves, indicating the deposition of an electrochemically active material on the electrode surface, was observed at 0.1 V/s. This behavior contrast with that found for the [Ru (5-Clphen)$_2$Cl]$^+$ derivative [29] where the electropolymerization was reductively induced by formation of phenanthroline radical after elimination of a chloride. Stable and electrochemically active poly-M(5-NO$_2$)TRP materials were deposited on the electrode surface, and characterized by electrochemistry, infrared spectro-electrochemistry and atomic force microscopy. The high electrochemical stability in aqueous and DMF solution were explored to develop sensor applications. In particular, the electrocatalytic activity of polymeric Ni-(5-NO$_2$)TRP for reduction of nitrite generating NH_2OH, N_2H_4, and NH_3 with turnover frequencies of 30.2, 4.2, and 7.1 s^{-1}, respectively, was reported for the first time.

That work was extended to the zinc(II) and free-base porphyrin derivatives, and the electrocatalytic activity of polymeric films demonstrated for reduction of nitrite [30] and sulfite in water/ethanol solution [31]. The modified electrodes prepared by successively cycling the potential in the −1.20 to 1.50 V range (50 times), exhibited high electrocatalytic activity for reduction of SO_2 at pH 1.0, which was significantly decreased at pH 3.5. The modified electrodes were explored as sulfite sensors in wine samples where the detection and quantification limits, respectively, of 1.40 and 4.68 mg/L were achieved for the polymeric Ni-(5-NO$_2$)TRP derivative. High selectivity and electrocatalytic activity for oxidation of gallic acid was also reported.

Nafion, a negatively charged sulfonated polymer, electrostatically loaded with positively charged cobalt tetraruthenated porphyrin, was explored as an alternative electrode material to the dip-coated and electrostatic-assembled M-(5-NO$_2$)TRP modified electrodes for amperometric detection of sulfite in wine model [32, 33]. The modified electrodes were prepared depositing a 1 % Nafion solution onto GC surface, letting it dry in air, then dipping into a 1 mM Co-(5-NO$_2$)TRP methanolic solution for 4 min, and rinsing with DI-water. The ethanol/water solution used as wine model was prepared with 0.02 M tartaric acid, 0.1 M $NaClO_4$, and 12 % ethanol, and the pH adjusted to 1.0 with $HClO_4$.

The GC/Nafion/Co-(5-NO$_2$)TRP modified electrodes were stable in water/ethanol solution and presented only a reversible Ru(III/II) pair of waves at 0.8 V versus Ag/AgCl in the −1.0 to 1.0 V range. However, an irreversible reduction wave, whose intensity is linearly dependent on sulfite concentration in the 0.4 to 70 mg/L range, appeared at $E_{pc} = -0.52$ V, confirming that tetraruthenated porphyrins continue to be electrocatalytic active for reduction processes. The detection and quantification limits were estimated as 0.4 and 1.2 mg/L, respectively. The electrolysis at −0.65 V for 6 h produced thiosulfate and not dithionite, the conventional reduction product in acidic media. The modified electrodes exhibited high stability, and 4.1 % was the RSD measured for 10 independent electrodes stored for 90 days in open air. Rotating disk voltammetry experiments showed a linear Koutecky-Levich plot and the electrocatalytic oxidation of sulfite was limited by electron diffusion through the film. In fact, because of the presence of Co-(5-NO$_2$)TRP dispersed in nonelectroactive Nafion, several processes such as (a) the mass transfer at film and electrode surface, (b) the electron and substrate diffusion



[4TPyP{Pt(bpy)Cl}$_4$] [4TPyP{Pt(bpy)Cl}$_4$]

Fig. 4 Structure of the *meta* and *para meso*-(tetrapyridyl)porphyrins coordinated to four [Pt(bpy) Cl]$^+$ complexes

rate through the film, and (c) the film/substrate electron transfer rate, can limit the current.

More recently, tetraplatinumpyridylporphyrins (Fig. 4) were synthesized by reacting H_2-3TPyP and H_2-4TPyP with [Pt(bpy)Cl_2] complex for 36 h, in trifluoroethanol, while monitoring spectrophotometrically the reaction progress [34]. The compounds were isolated as solids and characterized by spectroelectrochemistry. The UV–Vis spectra in the visible range were analogous to that of parent porphyrin species, whereas the absorption bands at 247, 307, 318, and 370 nm where assigned to the peripheral platinum complexes. Three redox processes were found at −1.5, −1.35, and 0.75 V versus Ag/$AgNO_3$, two reversible reductions and an irreversible oxidation process, respectively. The first oxidation and the first reduction processes were porphyrin centered whereas the second reduction was assigned to bpy/bpy$^-$ (and P$^{-/2-}$) process, in agreement with the four times higher current intensity as compared with the preceding wave. This assignment was confirmed by spectroelectrochemistry that essentially showed spectral changes in porphyrin bands.

The peripheral square planar [Pt(bpy)Cl(pyP)]$^+$ complexes intercalation properties into DNA were evaluated spectrophotometrically by UV–Vis absorbance and luminescence spectroscopy, as well as by SPR titration. The sharp decrease of the Soret band observed upon interaction with low concentrations of calf-thymus DNA, in parallel with the slight increase in luminescence indicated the predominance of the electrostatic interaction mode. However, a shift to intercalation mode was observed at higher concentrations, as confirmed by the typical red shift of the Soret band associated with a large enhancement of luminescence. The interaction was also monitored by surface plasmon resonance spectroscopy. A SAM of cysteamine was deposited on gold SPR sensors generating a positively charged layer of protonated amine groups. Calf-thymus DNA was electrostatically bound onto, and the modified surface interacted with the [TPyP{Pt(bpy)$_2$Cl}$_4$]$^{4+}$ complex. A contrasting

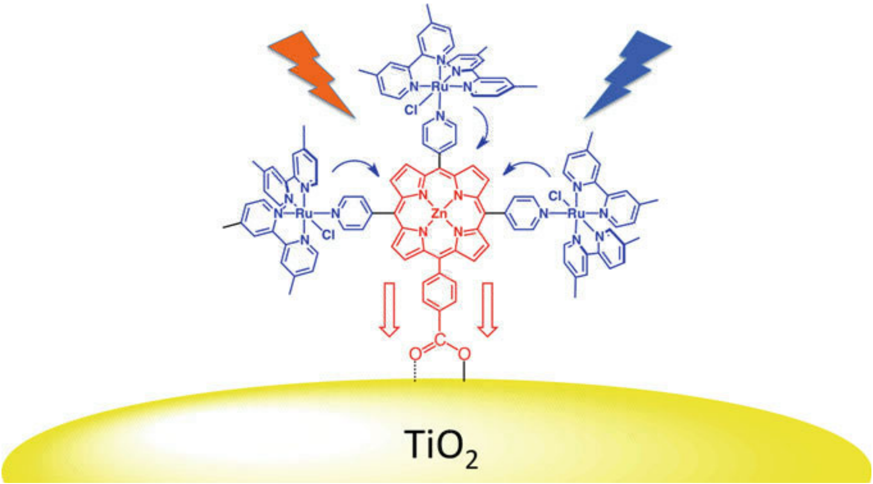
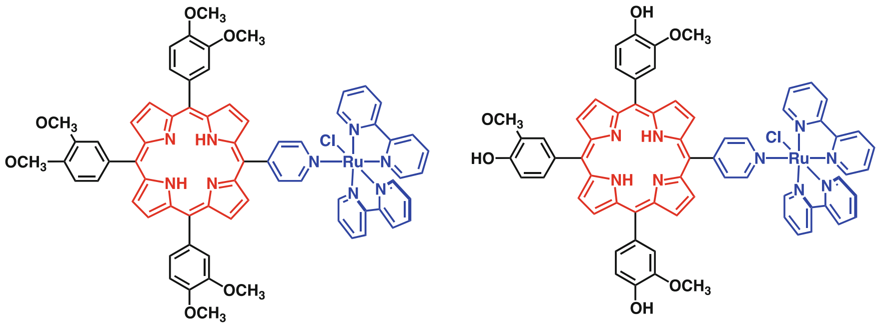


Fig. 5 Scheme showing the supramolecular Zn-MCTPyPRu$_3$ dye anchored on a TiO$_2$ surface. Electron injection or energy transfer (ET) takes place from the peripheral ruthenium complexes after photoexcitation of the zinc(II) porphyrin tetrad enhancing the electron injection to the mesoporous semiconductor and the charge separation efficiency at the interface

behavior was observed for the 4-pyridyl and 3-pyridyl porphyrin derivatives, as expected from the planar and saddle-shaped structures. The *para*-substituted species interacted very weakly whereas the *meta*-substituted species exhibited a high binding affinity assigned to the prevalence of intercalation interactions with DNA major grooves, as confirmed by molecular modeling.

A new supermolecular porphyrin dye was prepared by coordination of three [Ru(dmbpy)$_2$Cl]$^+$ complexes (dmbpy=4,4′-dimethyl-2,2′-bipyridine) to 5-(4-carboxyphenyl)-10,15,20-tri(4-pyridyl)porphyrin and its zinc(II) complex, Zn-MCTPyPRu$_3$ [20]. This species was engineered in order to have a carboxyphenyl group as anchoring site on mesoporous TiO$_2$ surface, and [Ru(dmbpy)$_2$Cl]$^+$ as functional ancillary groups (Fig. 5) acting as effective antennas and redox sites transferring energy and electron to the porphyrin site. In fact, the peripheral ruthenium complexes are able not only to transfer energy but also to regenerate very rapidly the porphyrin sensitizer after electron injection to TiO$_2$, taking the oxidized equivalent away from the semiconductor surface and slowing down the electron-hole recombination process. The photo action spectrum showed a broad and strong band around 500 nm, absent in the parent porphyrins, reflecting the high contribution of peripheral complexes to the photocurrent. The I–V curves showed reproducibly the superior response of the triruthenated porphyrin dyes increasing the quantum efficiency from 0.11 to 0.77 in the zinc porphyrin tetrad. In this way, a supramolecular photosensitizer with efficient antenna effect was realized, exhibiting up to seven fold larger photoelectrochemical efficiency as compared to the parent zinc(II)*meso*-tetra(pyridyl)porphyrin species.



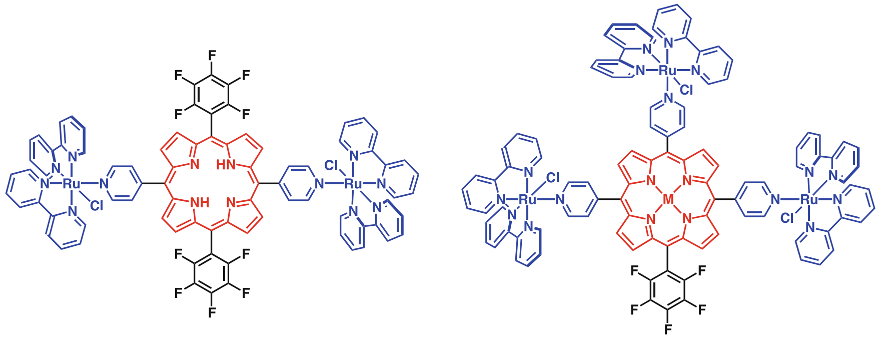
[H_2-MPy3,4DMPP(Ru(bpy)$_2$Cl)]

[H_2-MPy3M4HPP(Ru(bpy)$_2$Cl)]

Fig. 6 Structure of supramolecular porphyrin species [H_2-MPy3,4DMPP(Ru(bpy)$_2$Cl)]$^+$ and [H_2-MPy3M4HPP(Ru(bpy)$_2$Cl)]$^+$

Two new porphyrin derivatives, *meso*-tris-(3,4-dimethoxyphenyl)-mono-(4-pyridyl)porphyrin (H_2-MPy3,4DMPP) and *meso*-tris-(3-methoxy-4-hydroxyphenyl)-mono-(4-pyridyl)porphyrin (H_2-MPy3M4HPP), as well as the respective supramolecular species obtained by coordination to [Ru(bpy)$_2$Cl]$^+$ complexes (Fig. 6), were prepared by Marek et al. [35] and characterized by spectroelectrochemistry. The idea was improving the mechanical properties while decreasing the solubility of the ruthenated porphyrin films by electropolymerization through the 3,4-dimethoxyphenyl and 3-methoxy-4-hydroxyphenyl substituents, keeping the electrocatalytic and photochemical properties of the ancillary ruthenium polypyridine complex. The CV of [H_2-MPy3,4DMPP(Ru(bpy)$_2$Cl)]$^+$ species exhibited a reversible pair of waves at $E_{1/2}$ = 0.96 V assigned to the Ru(III/II) redox pair, and an irreversible wave at 1.22 V assigned to the oxidation of peripheral dimethoxyphenyl substituents, followed by a second irreversible oxidation of the porphyrin ring. Going to the negative side, a reversible wave was observed at −0.92 V, assigned to the porphyrin radical anion formation. The electrochemical behavior of the [H_2-MPy3M4HPP(Ru(bpy)$_2$Cl)]$^+$ species was similar but more easily oxidized and irreversible as expected from the presence of hydroxyphenyl substituents exhibiting acidic OH groups. The oxidative electropolymerization lead to the formation of electroactive materials in 0.5 M perchloric acid solution.

The [H_2-MPy3,4DMPP(Ru(bpy)$_2$Cl)]$^+$ species showed an emission band at 650–655 nm in acetonitrile [36] but the parent species exhibited a much higher quantum yield of 0.7 as compared with 0.04 of the ruthenated porphyrin species, indicating a strong quenching probably by electron transfer mechanism. Despite the presence of porphyrin and ruthenium bipyridine complex in the structure, the dyad did not exhibit electrogenerated luminescence by annihilation mechanism. However, in the presence of tri-*n*-propylamine (TPrA) at concentrations larger than 20 mM, an ECL was observed in all potential range at 656 nm. The maximum was reached at 0.9 V where both, porphyrin ring and ruthenium complexes, are



***trans*-[H_2-DPyDPFPP{$Ru(bipy)_2Cl$}$_2$]**

[H_2-TPyPFPP{$Ru(bipy)_2Cl$}$_3$]

Fig. 7 Structure of the *trans*-diruthenated and triruthenated *meso*-(pentafluorophenyl)(4-pyridyl)porphyrin derivatives, where M = $2H^+$ or Cu^{2+}

oxidized, suggesting the occurrence of multiple electron transfer processes before reaction with TPrA.

Trans-diruthenated [37] and triruthenated [38] *meso*-pentafluorophenyl (4-pyridyl)porphyrin derivatives (Fig. 7) were synthesized and their ability to interact with DNA explored aiming application in photodynamic therapy. The *trans*-[H_2-DPyDPFPP{$Ru(bpy)_2Cl$}$_2$]$^{2+}$ species exhibited reversible processes at 0.88, −0.68, and −1.11 V versus Ag/AgCl, respectively, assigned to the Ru(III/II), P(0/−), and P(−/2−) redox couples where P = porphyrin. An additional quasi-reversible wave, absent in the respective nonruthenated species, was found at $E_{1/2}$ = −1.42 V and attributed to the reduction of a bipyridine ligand to the respective radical anion. The triruthenated [H_2-TPyPFPP{$Ru(bipy)_2Cl$}$_3$]$^{3+}$ species exhibited a similar electrochemical behavior, showing the ruthenium- and porphyrin ring-centered redox processes that were confirmed by UV–Vis spectroelectrochemisty. The Ru(III/II) process was found at 0.88 V whereas the porphyrin was reduced to the radical anion at −0.79 and −0.86 V versus Ag/AgCl in DMF solution, respectively, in the free-base and copper(II) complex [38].

Those species interact with calf-thymus DNA with constants $K_b = 1.1 \times 10^5$ and $4.7 \pm 1.1 \times 10^4\ M^{-1}$, respectively, determined for the di- and triruthenated species using the equation

$$[\text{DNA}]/\left(\varepsilon_a - \varepsilon_f\right) = [\text{DNA}]/\left(\varepsilon_b - \varepsilon_f\right) + 1/K_b\left(\varepsilon_b/\varepsilon_f\right),$$

where ε_a = absorbance/[complex], ε_b and ε_f are the extinction coefficients, respectively, of the bond and free complex. The [H_2-DPyDPFPP{$Ru(bipy)_2Cl$}$_2$]$^{2+}$ species exhibited a large red shift of the Soret band, characteristic of intercalative binding, whereas the Soret band of the triruthenated species remained almost unchanged as expected for preferential electrostatic interaction with GC base pairs at the grooves. In addition, both were interacted with supercoiled DNA and irradiated with visible light from a 100 W mercury arc lamp, by filtering out high-energy photons with wavelengths below 400 nm. Interestingly, the triruthenated copper porphyrin showed higher photochemical activity. After 30 min of irradiation, all supercoiled plasmid was nicked through a mechanism involving molecular oxygen [38].

Furthermore, tetrachromium supramolecular porphyrin derivatives were prepared by Garcia et al. [39] by refluxing Fe-TPyP and Ni-TPyP with *trans*-$[Cr^{III}(phen)_2(TFMS)_2]^+$ complex and metallic zinc shots in methanol solution, where TFMS = trifluoromethanesulfonate and phen = 1,10-phenanthroline. The resultant polymetallic species has a labile TFMS anion bond to an axial position that is readily substituted by chloride; for example when the supramolecular porphyrin was precipitated as chloride from a LiCl-saturated acetone solution. The desired $[M\text{-}TPyP\{Cr(phen)_2Cl\}_4](PF_6)_8$, where M = $2H^+$, Ni^{2+}, and Fe^{2+}, where obtained after anion exchange and precipitation in NH_4PF_6 methanol solution (Fig. 8). Those compounds were characterized by spectroscopic and electrochemical methods where a quasi-reversible Cr(III/II) and two monoelectronic reduction processes centered on the porphyrin ring were observed in the CVs. Their UV–Vis spectra were essentially identical to those of the corresponding metalloporphyrins since the molar absorptivity of peripheral chromium phenanthroline complexes *d*–*d* transitions are much weaker than that of porphyrin π–π* transitions. In fact, only the strong phenanthroline intraligand π–π* transition is easily detected at 210 nm, whereas the band at 270 nm (π–π*) and the new Cl-to-Cr(III) ligand-to-metal charge-transfer transition band barely were noticeable. As expected, this band was shown to be sensitive to the metal ion coordinated to the porphyrin ring, shifting bathochromically from 327 to 364 nm when nickel(II) was replaced by iron(II) [39]. The $[Fe\text{-}TPyP\{Cr(phen)_2Cl\}_4]^{8+}$ species exhibited quasi-reversible redox waves at −0.29, −0.74, and −0.89 V while the respective nickel derivative presented those same redox processes at −0.39, −0.94, and −1.14 V. The first one was assigned to a Cr(III/II) redox process because of its much higher current intensity as compared to the other two waves, as expected for the relative number of peripheral chromium complexes to M-TPyP subunit (4:1 ratio). A careful spectroelectrochemistry study

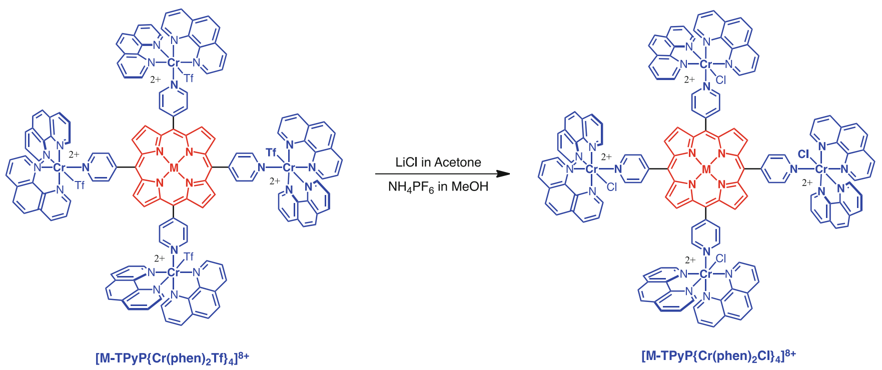


Fig. 8 Scheme showing the preparation of $[M\text{-}TPyP(Cr(phen)_2Cl]^{8+}$ from $[M\text{-}TPyP(Cr(phen)_2Tf]^{8+}$, where Tf = $CF_3SO_3^-$ anion

was carried out showing a more complex behavior probably reflecting the dissociation of labile Cr(II) complexes.

In fact, it is well known that Cr(III) polypyridyl complexes are reduced to the labile Cr(II) species upon irradiation with 351 nm laser, in agreement with their strong oxidant character in the excited state. Flash-photolysis experiments showed transient decay constants in the μs and sub-μs timescale that could be quenched by both, oxidants ($[Ru^{III}(NH_3)_6]$) and reductants (I^-, triethanolamine and alcohols) [39]. A very complex photophysic and photochemical behavior were described.

Another interesting class of peripherally metallated porphyrins are ferrocene-substituted species, previously reviewed by Bucher et al. [40] (Fig. 9). Ferrocene is known for their electron-donating and redox properties but the degree of electronic coupling with the porphyrin ring will depend on how they are linked with, i.e., (a) directly to the *meso*-positions, (b) by a conjugated or saturated bridging group, or (c) by a noncovalent interaction. The ferrocenyl groups directly bond to porphyrin *meso*-positions interact strongly generating class II mixed-valence species where each Fe(III/II) redox process can appear as separate waves in the cyclic voltammograms, instead of as one wave with intensity proportional to the number of appended ferrocenyl groups.

Typically, those ferrocenyl-porphyrins have been explored in photoinduced electron transfer and charge separation processes mimicking the activity of the photosynthetic system, as well as in the development of catalysts for multielectron transfer reactions. Ferrocenyl substituents were shown to enhance the electrocatalytic activity of cobalt [41, 42], iron [43], and copper [44–46] porphyrins for tetraelectronic reduction of dioxygen to water.

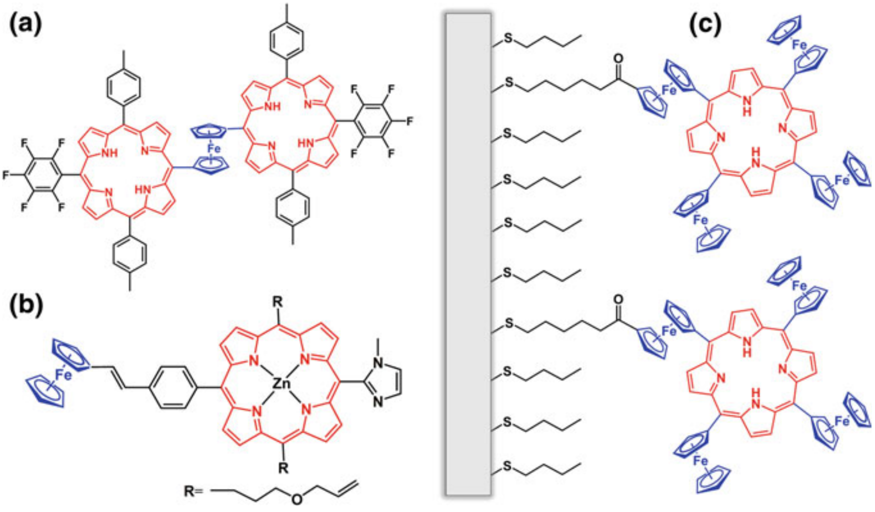


Fig. 9 Scheme showing **a** a bis-porphyrin connected by ferrocene core [40]; **b** a zinc porphyrin with a *meso*-methyl-imidazolyl substituent and possessing an appended ferrocenyl as electron donor group; [52] and **c** a scheme of a mixed SAM of 1-butanethiol and 5-[1′-(6-thioacetylhexanoyl) ferrocenyl]-10,15,20-triferrocenylporphyrin on gold surface [49]

Sun et al. [47] prepared a series of cobalt *meso*-(4-tolyl)(ferrocenyl)porphyrins with none to four ferrocenyl substituents bound directly to the *meso*-positions, and studied the influence of the bridging group on their electrochemical and electrocatalytic properties for the tetraelectronic reduction of dioxygen to water by cyclic voltammetry, rotating disk (RDE), and rotating ring-disk (RRDE) voltammetry. They exhibited two monoelectronic processes localized on the porphyrin ring at −0.81, −0.92, and −1.97 V in DMF solution. Note that the first reduction, assigned to the Co(II/I)P reaction, is cathodically shifted as the number of ferrocenyl groups increase from zero to four, whereas the potential for formation of Co(I)P π-radical anion remained almost unchanged. Going to the positive side, the first oxidation process was attributed to the Co(III/II)P redox couple which shifted cathodically from E_{pa} = 0.45 V to 0.30, 0.25, and 0.15 V while the Soret band red shifted from 432 to 448 nm as the number of peripheral complexes increased from 1 to 4, reflecting the electron-donating properties of ferrocenyl groups. The low reversibility of that process was assigned to the number of DMF molecules axially coordinated to the metalloporphyrin center that increased from one to two upon oxidation. That process is followed by oxidation of the ferrocenyl groups in the 0.56 to 0.59 V range, and a second process at 0.72 V for the tri- and tetra-substituted species. The oxidation of the peripheral groups to Fe(III) state change their initially electron-donating character to electron-withdrawing character, thus shifting anodically the porphyrin/porphyrin π-radical cation redox potential.

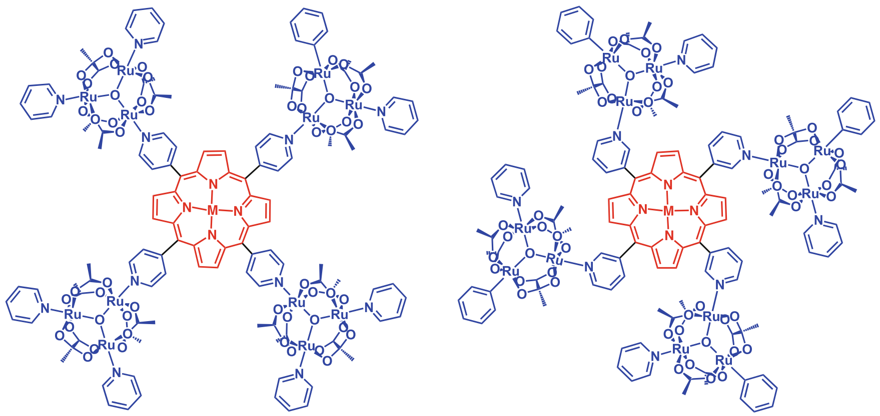
A cathodic wave assigned to the Co(III/II) process was observed at E_{pc} = 0.07, 0.20, and 0.14 V at 50 mV/s, for the CoP derivatives with zero, one, and three ferrocenyl substituents at the *meso*-positions [47], in 1.0 M $HClO_4$ electrolyte solution. This cathodic peak was enhanced after bubbling air into the solution as expected for the electrocatalytic reduction of O_2 to H_2O_2 or H_2O. Unfortunately, the peripheral ferrocenyl groups cannot transfer electrons to the active $Co^{II}P$ site, acting exclusively through electronic effects to change the reaction mechanism. Interestingly mono, tri, and tetraferrocenyl species adsorbed on electrode surface produced only H_2O_2 whereas the tetratolyl species transferred a higher number of electrons (n = 2.8) according to Koutecky-Levich analyses of RDE voltammograms. This suggested the operation of a tetraelectronic reduction pathway, as confirmed by RRDE voltammetry in analogous experimental conditions. The nonplanar geometry of ferrocenyl-substituted porphyrins inhibiting their π-stacking and dimerization probably is responsible for that result.

An attempt to improve the electron transfer properties of *meso*-tetra (ferrocenyl) porphyrins were carried out by incorporating fullerene in a composite material aiming application particularly in solar cells and photovoltaics [48, 49]. Also, the transition metals were replaced by In(III) that is able to coordinate one more axial ligand such as Cl^-, OH^-, and a η^1-ferrocenyl group improving its redox properties. The electrochemical studies carried out in DCM, using tetrabutylammonium tetrakis-(perfluorophenyl)borate (TBAF) as the electrolyte to avoid solute–electrolyte ion-pairing, resulted in voltammograms (CV, DPV, and SWV) exhibiting more or less well-resolved waves for each of the redox processes associated with all four ferrocenyl moieties in the −0.3 to 0.6 V range. A well-resolved monoelectronic wave was found at −0.13 V, clearly indicating the relatively strong electronic coupling among them. As expected, the mixed-valence species (classified as class II of Robin and Day) [50, 51] showed a broad intervalence transition band at 945–950 nm upon oxidation of the first ferrocenyl moiety. A new IVCT band appeared at 1150–1200 nm after oxidation of the remaining peripheral groups. In addition, two reversible porphyrin-centered monoelectronic processes were found at −1.6 and −2.4 V, as well as an irreversible ring oxidation process at 1.5 V. Large monocrystals potentially useful for the preparation of photovoltaics were obtained by co-crystallization with C_{60}.

A series of slipped cofacial zinc(II)porphyrin dimers formed through axial coordination of a *meso*-methyl-imidazolyl substituent and possessing an appended ferrocenyl as electron donor groups were realized as photosynthetic models (Fig. 9b) [52]. Directly bond and methyl-bridged ferrocene derivatives show good electronic coupling whereas phenylene-ethylene and phenylene-ethynylene spacers decreased the electronic communication. Those electronic effects were reflected on the absorption and fluorescence properties, as well as on the porphyrin ring redox properties.

More recently, unsymmetric *meso*-tetra(ferrocenyl)porphyrins with one FcCOR ferrocenyl complex substituted with pendant alkyl chain, where R=CH_3 (**1**), $(CH_2)_5Br$ (**2**), and $(CH_2)_5SCOCH_3$ (**3**), were synthetized and the electron transfer kinetics at the SAM/gold-electrode interface investigated aiming photoelectrochemical applications [49]. Stable mixed SAM of 1-butanethiol and 5-[1′-(6-thioacetylhexanoyl)ferrocenyl]-10,15,20-triferrocenylporphyrin (Fig. 9c) were formed on gold but the electrochemical processes were not well resolved as in solution, showing a broadened pair of waves. When irradiated with visible light, the same SAM modified electrode reduced dioxygen molecules dissolved in aqueous solution at 0.0 V. Photocurrent was generated when the highly reducing excited porphyrins ($E_{1/2}^* = -2.68$ V versus Ag/AgCl) transferred electrons in a nonreversible way to that sacrificial oxidizing species. However, its efficiency was shown to be rather low and tuned by the supporting electrolyte. Indeed, the bulky tetrakis (pentafluorophenyl)borate anion quenched the photocurrent since its diffusion into the monolayer is slow and insufficient to stabilize the oxidized porphyrin formed after photoinduced reduction of O_2 [49].

The series of tetracluster porphyrins was complemented by the preparation of the saddle-shaped 3-TPyP derivative by Formiga et al. [53]. The coordination of [μ-$ORu_3(CH_3CO_2)_6(py)_2$] complexes to the four *N*-pyridyl atoms produced a nonplanar H_2-3TCP species with a diminished π-electronic coupling as compared to the more symmetric H_2-4TCP species (Fig. 10). The electrochemical behavior of both isomers is dominated by the triangular ruthenium cluster moieties in contrast with the UV–Vis spectra where the porphyrin moiety shows up. Both species presented photoelectrochemical properties when adsorbed on mesoporous TiO_2 film and assembled in dye-sensitized solar cells. However, a new band around 670 nm seems to be contributing with photocurrent generation only in the *para*-isomer, reflecting the higher electronic coupling between the porphyrin and ruthenium cluster moieties.



[H_2-4TCP] **[H_2-3TCP]**

Fig. 10 Scheme showing the molecular structures of H_2-4TCP and H_2-3TCP species

Dyads based on triruthenium acetate cluster of formula $[Ru_3O(OAc)_6(CO)(py)$-pz-$Ru_3O(OAc)_6(CO)L]$, where L=pyridine derivatives, exhibit very large comproportionation constants ($K_c = 6.0 \times 10^7$ for L = dmap) indicating a highly stabilized mixed-valence state [54]. Accordingly, two intervalence charge-transfer (IVCT) bands were observed in the electronic absorption spectra of the singly reduced mixed-valence species and assigned to metal-to-bridge and metal-to-metal transitions. The degree of electronic delocalization is tuned by the L ligand and decrease in the following order: 4-dimethylaminopyridine (dmap) > pyridine (py) > 4-cyanopyridine (cpy). Those characteristics are very interesting to enhance the electrocatalytic and photoelectrochemical properties of a supramolecular system, and were used to expand the series of ruthenium cluster porphyrins [54]. In fact, a new mixed-valence species was prepared by bonding that pyrazine-bridged triruthenium cluster dimer to *meso*-triphenyl(4-pyridyl)porphyrinate zinc(II), Zn-TPPpy. The resultant $[Zn\text{-}TPPpy\{Ru_3O(OAc)_6(CO)\text{-}pz\text{-}Ru_3O(OAc)_6(CO)(py)\}]$ supermolecule (Fig. 11) exhibits seven reversible redox processes but no significant electronic coupling was found connecting the cluster dimer and the porphyrin ring. However, the S_1-excited zinc porphyrin is able to transfer an electron to the cluster dimer generating a mixed-valence charge-transfer excited state, as confirmed by the enhancement of the intervalence bands when irradiated at $\lambda_{exc} = 568$ nm.

Heteroarrays of porphyrins and phthalocyanines encompassing peripheral noncovalent and covalent bonding have been reviewed by Lo et al. [55] and Torres et al. [2] forming a variety of supramolecular structures. This class of compounds exhibits interesting spectroscopic, photophysical, and redox properties whose discussion was mainly focused in light-harvesting and optoelectronic device applications. Dyads were obtained by covalently linking the porphyrin *meso*-phenyl groups with the fused benzene ring of phthalocyanines using bridging groups such as ethers, amides, ethynyl, piperazine, etc. More complex systems were realized by