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Physicochemical Properties and Catalytic Applications of Iron Porphyrazines and Phthalocyanines

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Abstract

Porphyrazines and phthalocyanines belong to porphyrinoids, which are macrocyclic compounds consisting of four pyrrole or indole rings, respectively. The aromatic rings of porphyrazines and phthalocyanines are fused together by azamethine bridges (meso nitrogen atoms) in place of methine bridges present in porphyrins. The physicochemical properties of these macrocycles can be modified in two ways. The first is by substitution of metal cation in the core, whereas the second relies on peripheral modification with various substituents. Porphyrazines and phthalocyanines can be modified inside the macrocyclic core with various transition metal cations, including iron(II/III), which impacts their electrochemical properties and influences potential applications in redox reactions. Due to their unique optical and electrochemical properties, porphyrazines and phthalocyanines found many potential and practical applications in medicine and technology. They were mainly researched as photosensitizers in photodynamic therapy, as sensors in biomedical and analytical applications or as building blocks for materials chemistry. This chapter presents physicochemical properties and catalytic applications of iron porphyrazines and phthalocyanines. The first part summarizes the influence of peripheral and axial substituents of iron(II/III) porphyrazines and phthalocyanines on their spectral properties, whereas the second focuses on the electrochemical properties of these molecules. The third part covers the activity of selected iron(II/III) porphyrazines and phthalocyanines of potential value for diverse applications including catalytic reactions.

Keywords: catalytic properties, electrochemistry, iron, porphyrazines, phthalocyanines

1. Introduction to porphyrinoids

Porphyrinoids are macrocyclic compounds consisting of four pyrrole rings usually linked together through methine or azamethine bridges. Porphyrins (Ps) are planar and aromatic with nominally 22π-electrons of which 18π-electrons are engaged in a conjugative path. Porphyrins can be substituted at the peripheral β and methine meso positions. Chlorins and bacterichlorins possess similar structure to porphyrins, and they are defined as dihydro or tetrahydro derivatives of porphyrins. Corrole macrocycle constitutes an 18π-electron system with the characteristic feature being the lack of a methine bridge between the A and D pyrrole rings. In addition, corolles carry inside the macrocyclic core three NH protons, which is different from porphyrins and chlorins, which carry two NH protons. It is worth noting that structurally related corrins with the key natural product cobalamine (vitamin B_{12}) are not aromatic and contain only one NH proton inside the macrocyclic core. Porphyrazines (Pzs) and phthalocyanines (Pcs) commonly known as tetraazaporphyrins belong to synthetic porphyrinoids. Methine bridges are replaced by azamethine (with nitrogen atoms) as the most notable feature of their structure. In addition, Pcs are tetrabenzo tetraazaporphyrins, which have annulated benzene rings in comparison with the Pz core. Formally, in phthalocyanines, unlike in porphyrazines, the azamethine bridges combine four indole instead of pyrrole rings, respectively (**Figure 1**). The derivatives of Pcs can be obtained by substitution of fused benzo-rings at peripheral (2,3 or β) and nonperipheral positions (1,4 or α). The tetraazaporphyrins possess unique physicochemical properties due to the presence of a conjugated system of
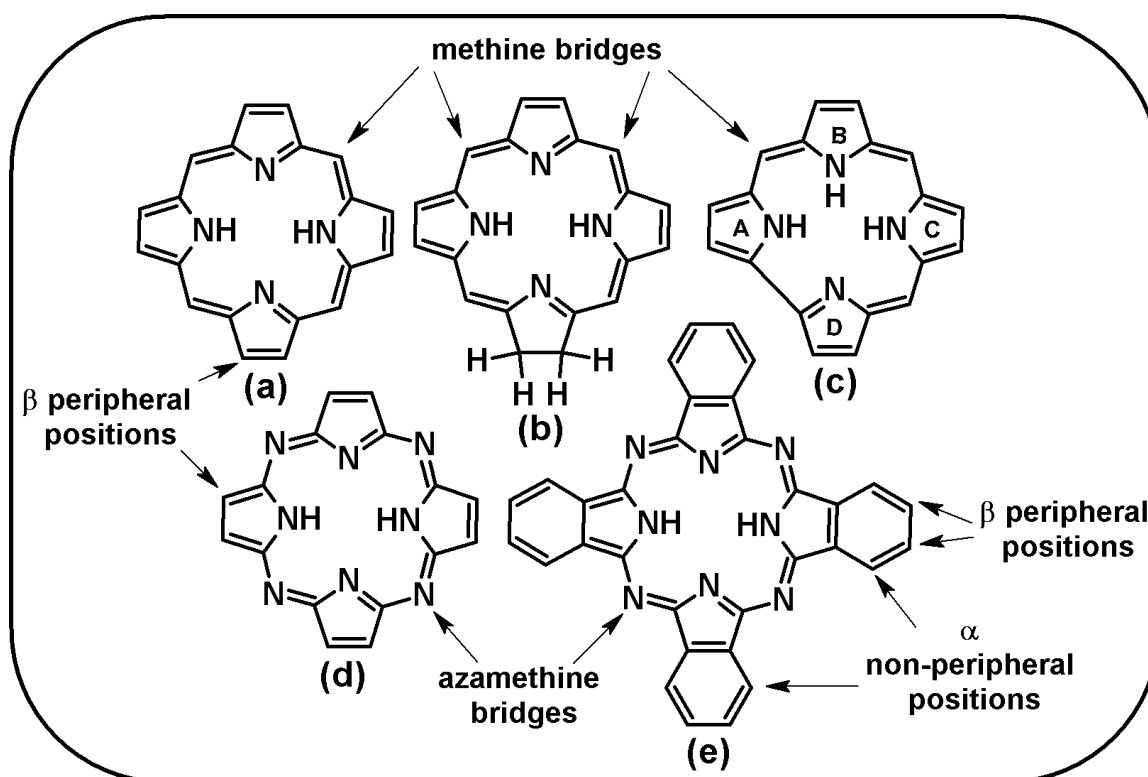

Figure 1. Structures of porphyrins (a), chlorins (b), corroles (c), porphyrazines (d), and phthalocyanines (e).

π electrons, bulky periphery and an ability to coordinate various metal cations inside macrocyclic core. The chelation reaction of the inner NH protons with various metal ions leads to metal chelates, which is a common feature for all porphyrinoids [1–6].

Many natural porphyrins and chlorins, for example, heme in hemoglobin and chlorophyll, reveal various vital functions and are responsible for many biochemical processes. Nowadays, porphyrinoids possess potential applications in science and technology, for example, synthetic derivatives of porphyrins as well as phthalocyanines found many applications in the dye industry and revealed potential for medicine (photodynamic therapy and photodynamic diagnosis) and technology (artificial enzymes, catalysts). Many tetraazaporphyrins have also been studied as analytical indicators, structural elements in materials chemistry, in optical data drivers and microchips, as well as photovoltaic cells. In addition, there is a possibility to utilize porphyrazines and phthalocyanines as catalysts in various organic synthesis reactions due to their ability to coordinate transition metal cations inside macrocyclic core or in the periphery. Lately, tetraazaporphyrins have also been considered as building blocks in nanotechnology due to their self-assembly and self-organization ability (**Figure 2**) [3, 6–19].

Tetraazaporphyrins can be modified using two approaches. The first relies on the introduction of various alkyl and/or aryl substituents with sulfur, nitrogen or oxygen atoms into porphyrazine β peripheral positions of pyrrole rings and phthalocyanine α nonperipheral and/or β peripheral positions of indole rings. The second concerns removal or exchange of central metal cation present in macrocyclic core. By using all of these modification approaches, there is a possibility to obtain macrocyclic compounds of altered physicochemical properties, for example, extended thermal and photochemical stability, increased solubility in organic solvents, improved luminescence and spectroscopic, magnetic, electrochemical properties, photoconductivity and surface activity [1, 2]. Incorporation of iron(II/III) cations into the porphyrinoid core allowed the application of these compounds as catalysts in redox reactions. There is a great interest in the catalytic properties of iron(II/III) tetraazaporphyrins, which dates back to the 1980s. These macrocyclic systems were considered as potential electron
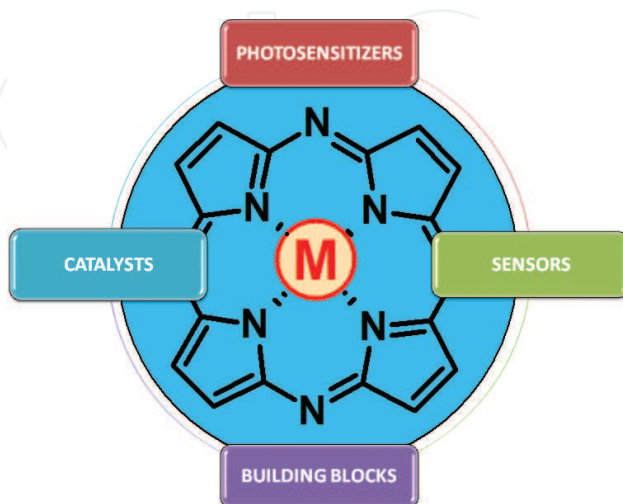

Figure 2. The main practical and potential applications of tetraazaporphyrins, M—metal ion.

and/or molecule carriers. For example, iron(III) octaphenylporphyrazine pyridine adduct developed by Stuzhin was found to be a molecular oxygen carrier [20]. Theoretical calculations using density functional theory (DFT) and experimental studies indicated that there are significant differences between metalated tetraazaporphyrins and porphyrins. The difference in the core size and shape of the macrocycle has a substantial effect on the electronic structure and properties of the overall system. DFT calculations indicated on differences in bond lengths between pyrrole/indole nitrogen atoms and coordinated iron(II) cation in porphyrins, phthalocyanines and porphyrazines, which were 1.98; 1.93 and 1.90 Å, respectively. The smaller coordination cavity results in a stronger ligand field in Pzs than in porphyrins. However, the benzo annulation in phthalocyanines produces a surprisingly strong destabilizing effect on the metal-macrocycle bonding [21, 22]. The calculations also showed how the differences in porphyrinoid (Ps, Pcs and Pzs) structures influence the axial ligand coordination of pyridine and CO to the iron(II) complexes [22].

2. Physicochemical properties of iron porphyrazines and phthalocyanines

2.1. Low solubility and tendency to form aggregates hampering utilization

Applications of porphyrazines and phthalocyanines in science and technology are limited by their low solubility in water and organic solvents and their tendency to form aggregates. These unwelcome features are the result of their likelihood to molecular interactions based on π-π stacking. Unfavorable common feature of iron(II/III) porphyrazines and phthalocyanines to form aggregates is mainly related to their conjugated, extended system of π-electrons and an ability of iron cation to coordinate compounds with heteroatoms. Annulation of a porphyrazine macrocyclic system with four benzene rings leads to a phthalocyanine with four indole rings of enhanced aggregation properties. Most of the iron(II/III) tetraazaporphyrins form two types of aggregates: *J*-type aggregates (*head to tail*) or *H*-type aggregates (*face to face*) [23, 24]. In addition, it was also observed that an incorporation of bulky substituents into iron(II) porphyrazine ring, which resulted in the separation of molecules at the distance of ca. 11 Å in the X-ray structure, did not prevent its tendency to form aggregates in solution [25].

Generally, the unsubstituted tetraazaporphyrins possess low solubility. For this reason, the most effective method applied for increasing their solubility is peripheral functionalization. Peripheral functionalization of these compounds with ester groups is able to increase their solubility in many organic solvents. For example, magnesium(II) porphyrazine with 4-hydroxybutylthio substituents was subjected to esterification reaction with 4-biphenylcarboxylic acid and further metalated with Fe^{2+} salt toward **1** (**Figure 3**). Unlike the parent demetalated porphyrazine, the metalated porphyrazines functionalized with eight ester groups were soluble in common organic solvents, such as chloroform, dichloromethane, tetrahydrofuran, acetone, and toluene and were insoluble in water and *n*-hexane [23].

Peripheral functionalization of iron(II/III) porphyrazines and phthalocyanines with halogen electron withdrawing groups (like -F or -CF$_3$) was found to improve their solubility in polar solvents like methanol or ethanol, ionization potential and their stability in catalytic
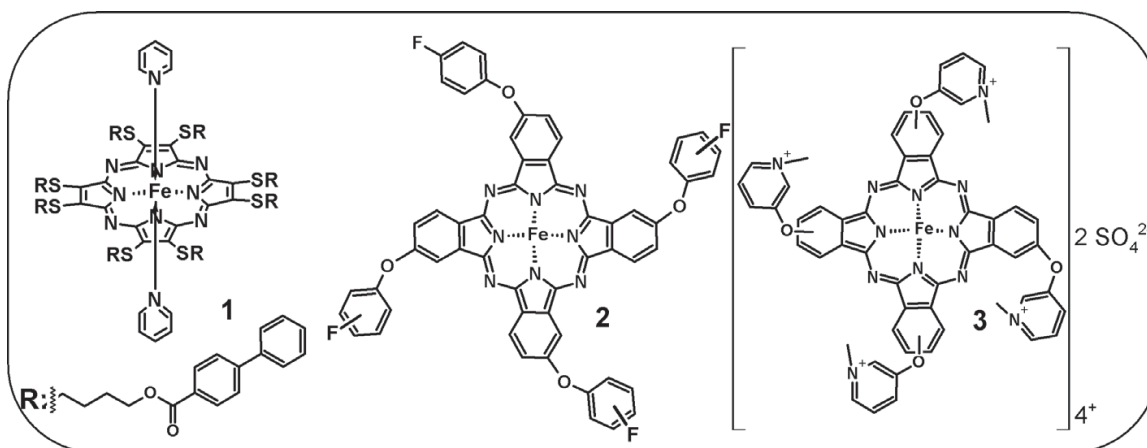
Figure 3. Structures of porphyrazine **1** and phthalocyanines **2** and **3**.

oxidation reactions [24, 26]. For example, iron(II) phthalocyanine with peripheral 4-fluoro-phenoxy groups **2** (**Figure 3**), which was synthesized using microwave-assisted cyclotetra-merization (much faster in comparison to classical method), revealed very good solubility in various organic solvents, thus allowing solvatochromic measurements. Unfortunately, this phthalocyanine formed *H*-aggregates as compared to demetalated phthalocyanine and other metalated phthalocyanines (CuPc, Li_2Pc), especially in polar solvents [24].

Over the years, many methods have been developed in order to obtain soluble tetraazapor-phyrins and to utilize them in aqueous media. This was a big challenge because as presented above these macrocycles are known for their aggregation properties. For this reason, a study was performed aiming to incorporate macrocycles into larger structures like β-cyclodextrines (β-CDs). For example, such complexes of β-CDs and iron(II) phthalocyanine **3** with peripheral quaternary pyridinium salt substituents were obtained in Kobayashi group (**Figure 3**) [27]. It is worth noting that the quaternization reaction was performed to enhance water solubil-ity. The addition of β-CD to the aqueous solution of **3** disturbed the monomer-dimer equi-librium, as was seen by an increase in the monomer band and a decrease in the dimer band absorbance in the UV-Vis spectrum. This inclusion complex was deposited on a glassy carbon electrode. In the cyclic voltammetry studies in aqueous solution, **3** revealed very good ability toward oxygen reduction reaction (ORR) at low potential values. It indicates that the "host" compound (β-cyclodextrine) has no influence on physicochemical properties of the "guest" compound (macrocycle).

2.2. Advanced physicochemical features

Iron cation coordinated inside a macrocyclic core of porphyrazines and phthalocyanines can be involved in redox reactions and influence their electrochemical properties. By changing the valence of central iron(II/III) metal cation in tetraazaporphyrins, it is possible to transfer electrons on diverse molecules. This feature concerns also axially coordinated compounds, which form enhanced complexes and can be divided into two types. To the first group belong small ions or molecules with heteroatoms in their structure, like pyridine, pyrazine or hydroxyl and bisulfate anions. The obtained complexes are formally named as the axial

complexes. To the second group belong dimers with single atom bridging groups between two iron macrocycles. In both cases, the obtained molecules have modified optical and electrochemical properties [28, 29].

A coordination of iron cation with proper ligand results in the formation of five- or six-coordinated macrocyclic complexes, which were subjected to broad study by Stuzhin et al. [28]. The coordination of iron(II) tetraazaporphyrins with axial ligands leads to the oxidation of iron(II) to iron(III). In this way, iron(II) octaphenylporphyrazine coordinated axially with F^-, Cl^-, Br^-, I^- and HSO_4^- anions was transformed to five-coordinated iron(III) complex **4** (**Figure 4**) [28, 30]. The spin state of the iron in this type of complex, which was evidenced for chloride complex, depended mainly on the nature of both the macrocyclic and axial ligands. In addition, when iron porphyrazine was coordinated with pyridine, the macrocyclic ligand adopted an intermediate structure between common porphyrins and phthalocyanines [30]. Iron(II) porphyrazines reversibly bind a variety of neutral ligands such as THF, nitrogenous bases, and carbon monoxide. This fact can be related to the higher π acidity of the porphyrazine ligand as compared to the porphyrin ligand. Iron(II) porphyrazine demonstrates no affinity for molecular oxygen, which can be a result of positively shifted III/II redox couple potential [31].

Another group of complexes, six-coordinated iron(II) complexes called bisaxial complexes also constitute a large group of compounds. DMSO, pyridine and pyrazine are one of the most often utilized molecules for coordination of iron cation, thus forming adducts as it was studied for iron(II) tetrakis(thiadiazole)porphyrazine **5** in Ercolani and Stuzhin groups (**Figure 4**) [32]. Coordinated bidentate molecules, for example, pyrazine, can be used as linkers between two or more macrocycles forming bridged complexes. What is more, the axial ligation of metalated Pz derivative with chloride influenced the Q-band absorption, which was the result of change in the symmetry from D_{4h} to C_{4v} [23]. FT-IR studies of iron(II) porphyrazine complex **5** axially coordinated with DMSO showed that two Fe-O coordination bonds
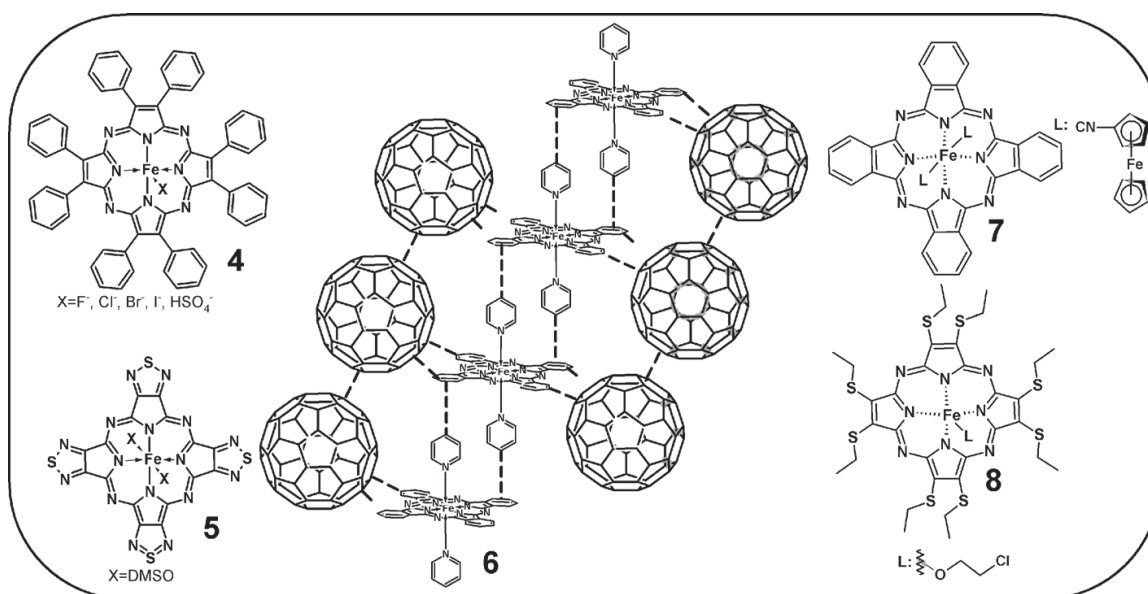

Figure 4. Chemical structures of iron(III) octaphenylporphyrazine **4**, iron(II) tetrakis(thiadiazole)porphyrazine **5**, crystal structure of **6**, phthalocyanine trinuclear molecular wire **7** and iron(III) porphyrazine **8**.

were formed. However, in phthalocyanines, analogical process was based on Fe-S coordination bond formation. It indicates that porphyrazine **5** is stronger π-acceptor [32].

Iron(II) phthalocyanines demonstrate the ability to form coordination assemblies with large structures like neutral and negatively charged fullerenes. An interesting example is crystal of **6** (**Figure 4**) obtained by cocrystallization from *n*-hexane and composed of fullerenes C_{60} and unsubstituted iron(II) phthalocyanines axially ligated with pyridines. In the structure of **6,** there are π-π stacking interactions, which do not affect the geometry of iron(II) phthalocyanine [33]. Thus, metal phthalocyanines can be involved simultaneously in molecular complexes with fullerenes as coordination assemblies and with the addition of axial ligands. Another example is trinuclear complex **7** (**Figure 4**) involving two isocyanoferrocene ligands axially coordinated to iron(II) phthalocyanine. The structure **7** forms a molecular wire between iron cation from phthalocyanine and two iron ions from ferrocenes. However, there is weak electronic communication present between two iron centers of the ferrocene ligands despite a relatively large distance (11.5 Å) [34].

An improvement in synthetic methods from the late 1980s allowed the obtaining of iron(II/III) porphyrazine and phthalocyanine complexes able to form dimers of macrocycles bridged by oxygen, nitrogen or carbon atoms (μ-oxo, μ-nitrido and μ-carbido dimers, respectively). Electrochemical studies demonstrated that macrocyclic ligand can influence the redox behavior of the binuclear complex. According to Colomban et al., dimer consisting of two porphyrazines possesses intermediate properties between corresponding porphyrin and phthalocyanine dimers [29]. This statement is based on the observation that the values of half-waved oxidation potentials of porphyrazine dimer were in the middle between similar phthalocyanine and porphyrin potentials, and for this reason, oxidation potentials in porphyrazine-based complexes are closer to phthalocyanines than porphyrins. Cyclic voltammetry of monomeric iron(III) porphyrazine axially ligated with 2-chloroethoxy substituent **8** (**Figure 4**) and its μ-oxo dimer demonstrated in DMF/TBAP three and six redox processes, respectively. Thus, the redox behavior of μ-oxoporphyrazine dimer differs significantly not only from that of the small ring system of μ-oxoporphyrin dimer, but also from that of the large-ring based μ-oxo dimer of phthalocyanine [35]. Compound **8** was also used for thin film formation utilizing Langmuir-Schaefer (LS) technique (horizontal lifting) following the study presented by Garramone et al. [36]. In aqueous solution, the μ-oxo dimer was formed as a predominant component (prevalent molecular building block) of LS films. The obtained LS-Fe films showed remarkable changes in the UV-Vis spectra, which are consistent with a significant μ-oxo dimer to monomer conversion [36]. The studies on μ-oxo iron phthalocyanine dimer demonstrated that according to the reaction conditions, it is possible to obtain bent or linear Fe-O-Fe structures (with Fe-O-Fe angle up to 300°). These two forms were identified by FT-IR signals from Fe-O antisymmetric stretching vibration. Moreover, it was possible to transform bent into linear form by applying the following reaction conditions: (i) by adding of 2-propylamine to compound suspended in chloronaphthalene or (ii) by the mixing the compound in the saturated H_2SO_4 solution in the presence of oxygen [37].

In comparison with well-known classic alone atop the other dimer structures, there is an example of significantly different "side-by-side" dimer structure **9** (**Figure 5**), which was considered as a novel molecular QCA (*quantum-dot cellular automata*) cell [38]. This dimer has
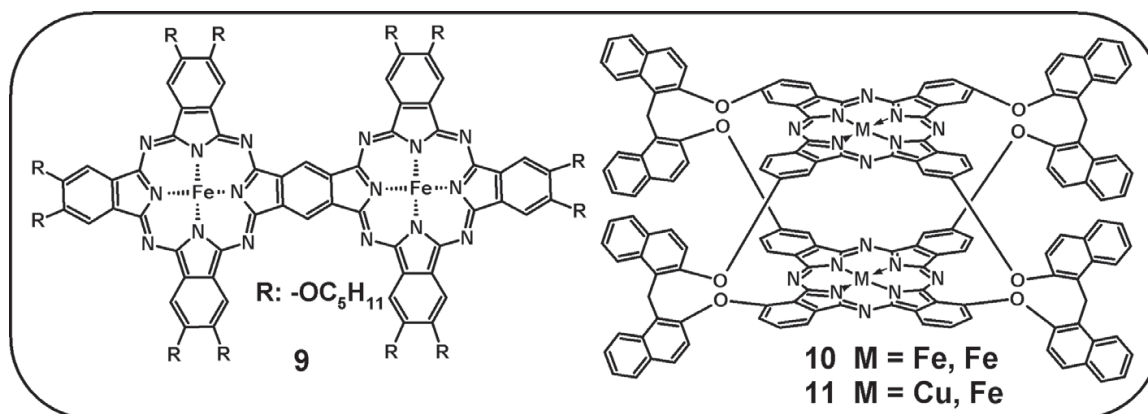
Figure 5. Structure of side-by-side dimer **9** and homonuclear and heteronulear dimers **10** and **11**.

pentyloxy substituents in the periphery, which results in its high solubility in organic solvents. The investigation of the redox properties of **9** in electrochemical study indicated that its oxidized and reduced mixed-valence complexes were stable [38]. Another of two tetraazaporphyrin macrocycles conjugated peripherally by 4,4'-[1,1'-methylenebis-(naphtalene-2,1-diyl)] bis(oxy)diphthalo-nitrile linker constitutes homonuclear (Fe-Fe) **10** and heteronuclear (Fe-Cu) **11** ball-type compounds (**Figure 5**). In both compounds, two phthalocyanine units were rigidly bound at two sides with four linking arms to form intramolecular cofacial coupling in which the splitting of the classical monophthalocyanine redox processes was observed in a cyclic voltammetry study. Moreover, the nature of the metal centers affected the distance between two Pc units in both ball-type complexes and thus the extent of the mentioned intramolecular cofacial interactions between them [39, 40].

3. Catalytic activity and electrochemical properties of iron porphyrazines and phthalocyanines

The presence of iron(II/III) cation in the coordination center of porphyrazine and phthalocyanine macrocycles determines the possibility of using them as catalysts of the oxidation-reduction reactions. Research studies carried out for several years showed that the iron tetraazaporphyrins are efficient catalysts as compared to the structurally similar porphyrin compounds. Porphyrinoid catalysts, also called biomimetic catalysts, are also more effective in carrying out the oxidation reactions of organic compounds, in comparison with other catalysts. It is related to the increased influence of the electron-donor effect of the ferric cation, which is conjugated to the π-electron system of the macrocyclic ring. The advantages of iron(II/III) porphyrazines and phthalocyanines as catalysts include high selectivity, mild and environmentally friendly reaction conditions and low energy consumption during catalysis [41]. In an early 1990s, Fitzgerald et al. provided various studies indicating significant differences in physicochemical properties of Ps, Pcs and Pzs possessing the same peripheral substituents and iron(III) cation inside a macrocyclic core [42]. It was suggested that porphyrazines are stronger σ-donors and π-acceptors than porphyrins. The electrochemical

studies indicated that similarly to phthalocyanines, porphyrazines have positively shifted redox potential of 400 mV in comparison with their porphyrin analogues. Moreover, Pzs are more soluble in organic solvents than structurally relevant Pcs and can split the d orbitals of coordinated metal to a greater extent than Ps. In conclusion, it was suggested that, due to the high solubility in organic solvents, accompanied by coordination of metal ions with unusual spin states, and positively shifted redox potentials, Pzs can be considered as more efficient catalysts in comparison with Ps and Pcs [42]. Taking all this into account, iron(II/III) tetraaza-porphyrins became an object of intense studies aimed at obtaining macrostructures with increased catalytic abilities. For instance, large structures like porphyrin-phthalocyanine pentads composed of five fused macrocyclic compounds **12** were even synthesized by Kobayashi et al. (**Figure 6**) [43]. Noteworthy is that the bimetallic Fe-Cu complexes, like metal-linked face-to-face porphyrazine dimer **13** with an increased strong metal-metal spin coupling, were obtained by Barrett, Hoffman and their coworkers [44].

Iron(II/III) porphyrazines and phthalocyanines are active in redox reactions and, therefore, reveal high electrochemical activity. This feature was confirmed by cyclic voltammetry (CV) and square wave voltammetry (SWV) studies, which show, in most cases, four reversible or quasi-reversible oxidation and reduction peaks. The origin of the two peaks was attributed to reactions associated with the presence of iron cation, whereas the other two are the
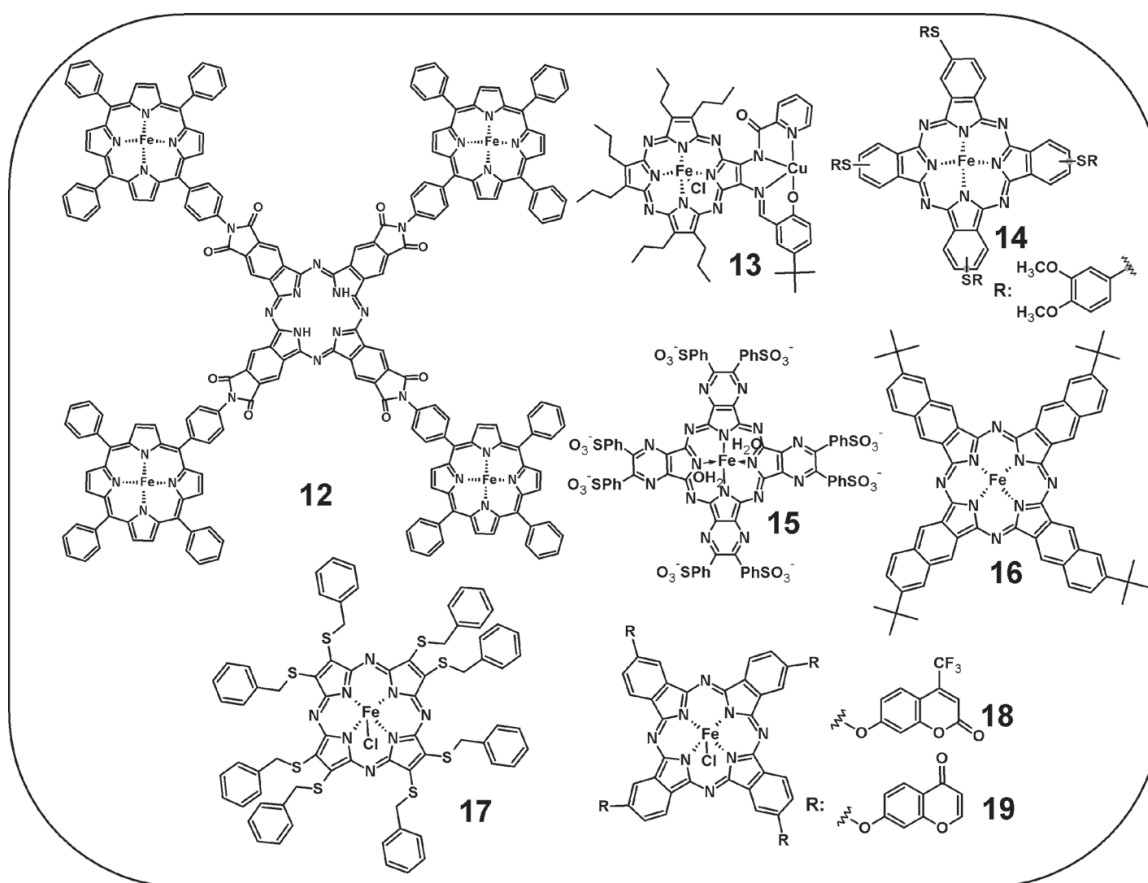

Figure 6. Structures of pentad **12**, bimetallic complex **13**, iron(II) phthalocyanine **14** and porphyrazine **15**, iron(II) naphthalocyanine **16**, iron(III) porphyrazine **17** and iron(III) phthalocyanines **18** and **19**.

result of the electronic processes within the macrocyclic ring [45]. However, there are some exceptions to this rule. For example, in the CV study performed in organic solvents for iron(II) phthalocyanine **14** (**Figure 6**), the presence of six oxidation-reduction processes was observed. Two of them were identified as reversible and irreversible reductions, while the other two were found to be quasi-reversible oxidation reactions [46]. In contrast to other iron porphyrazines, cyclic voltammetry study of water-soluble iron(II) porphyrazine **15** revealed no peaks observed for the Fe^{II}/Fe^{I} couple, probably as a result of slow heterogeneous electron transfer kinetics for this couple. Moreover, replacing of water in the coordination sphere of **15** by N-donor ligands increases the extinction coefficients of both the Q and Soret bands with a blue shift of the first one [47].

Electrochemical properties of iron(II/III) porphyrazine and phthalocyanine complexes are influenced by the periphery of the macrocycle, which can lead to an increase or a decrease of their electrochemical activity. An increase in activity is related to the presence of the peripheral substituents with lone pairs of electrons or π-electron systems, which are able to increase the coupling of electrons around the macrocycle. The decrease in activity is observed in the presence of electrochemically inactive substituents, for example, *tert*-butyl groups, as was found for iron(II) naphthalocyanine **16** (**Figure 6**) [48].

An axial coordination of molecules to the central metal ion can cause a shift of the oxidation potential of the macrocycle or a split of peaks belonging to oxidation process. The rationale for this may be connected with the coordination of solvent molecules to Fe^{3+} cation in the center of the oxidized macrocyclic compound [49]. It is known from the literature that there are differences in the values of oxidation-reduction potentials of iron phthalocyanines, when one or two solvent molecules are attached or released from the iron(II/III) cation [50].

Electrochemical studies with iron porphyrazines and phthalocyanines were also carried out using the modified electrodes with tetraazaporphyrins deposited on their surface. One example is the use of iron(III) porphyrazine **17** (**Figure 6**) as an azide and nitrate(III) anions sensor [51]. This porphyrazine was deposited onto a matrix with PVC, and the selective electrode membrane revealed a shorter electrode response time, greater tolerance within a wide range of pH at high analyte concentration and a high selectivity toward the targeted ions [51]. Another example is iron(III) phthalocyanine with four peripheral coumarin **18** or chromone **19** substituents (**Figure 6**) deposited by the electropolymerization on the Pt-working electrodes and applied as electron mediators in the electrocatalytic oxidation of nitrates(III) [52].

Studies concerning catalytic properties of iron porphyrazines and phthalocyanines have been conducted over the last 20 years, and they concerned mostly the potential applications in oxidation reactions of linear and cyclic alkenes as well as photocatalytic degradation of organic dyes. However, unsubstituted iron(III) phthalocyanine was widely used to catalyze the reaction of both the incorporation of amino substituents and the hydroxylation of aryl and alkyl molecules [53, 54]. Moreover, this compound was also used as a catalyst in the oxygen reduction reactions and revealed good stability for potential use in fuel cells or batteries [55, 56]. Some studies assessed the ability of iron(II/III) tetraazaporphyrins and their dimers in decomposition and removal of organic pollutants from industrial wastes. So far the most successfully applied photocatalytic reaction was the degradation of Rhodamine B,

which was considered as a model compound in studies on environmental contamination with organic substances. The most commonly used catalysts applied were symmetrical iron sulfanylporphyrazines **20**, **21** and **22**, as well as unsymmetrical **23** (**Figure 7**). They were used either as homogeneous or heterogeneous catalysts, after deposition on the carrier, which was very often ion exchange resin (e.g., Amberlite CG400). It was shown that the deposition of the catalyst on this kind of support increases the efficiency of catalytic reactions due to an increase in the concentration of catalysts on the resin surface. Therefore, the molecules of the substrate are present in high concentration in the vicinity of the catalyst, facilitating the oxidation and reduction reactions. In addition, it was shown that the iron(II) porphyrazine—resin system is active even in the dark, without activation of macrocycle by irradiation with proper wavelength [57]. Noteworthy, some oxygen atom donors (OAD) like molecular oxygen and hydrogen peroxide were added to the reaction mixture to form an active oxygen species, which allowed the oxidative degradation of substrates. The highest reaction rate and yield were achieved with H_2O_2 [58]. It was also noticed that the modification of peripheral groups of the macrocycle by introducing hydroxymethyl substituents demonstrated an increased solubility of the catalyst in water and in organic solvents [41]. In order to improve the catalytic properties, the structure of the macrocycle was equipped with electron donor methyl moieties [59].

Another sulfur iron(II) porphyrazine **24** (**Figure 7**) was used in the catalytic oxidation reaction of organic compound, that is, X3B dye (*Reactive Brilliant Red*). The reaction was provided with hydrogen peroxide as OAD and with simultaneous exposure to light. The catalyst was active in a broad temperature and pH range, with the best yield at pH = 2, and at the higher
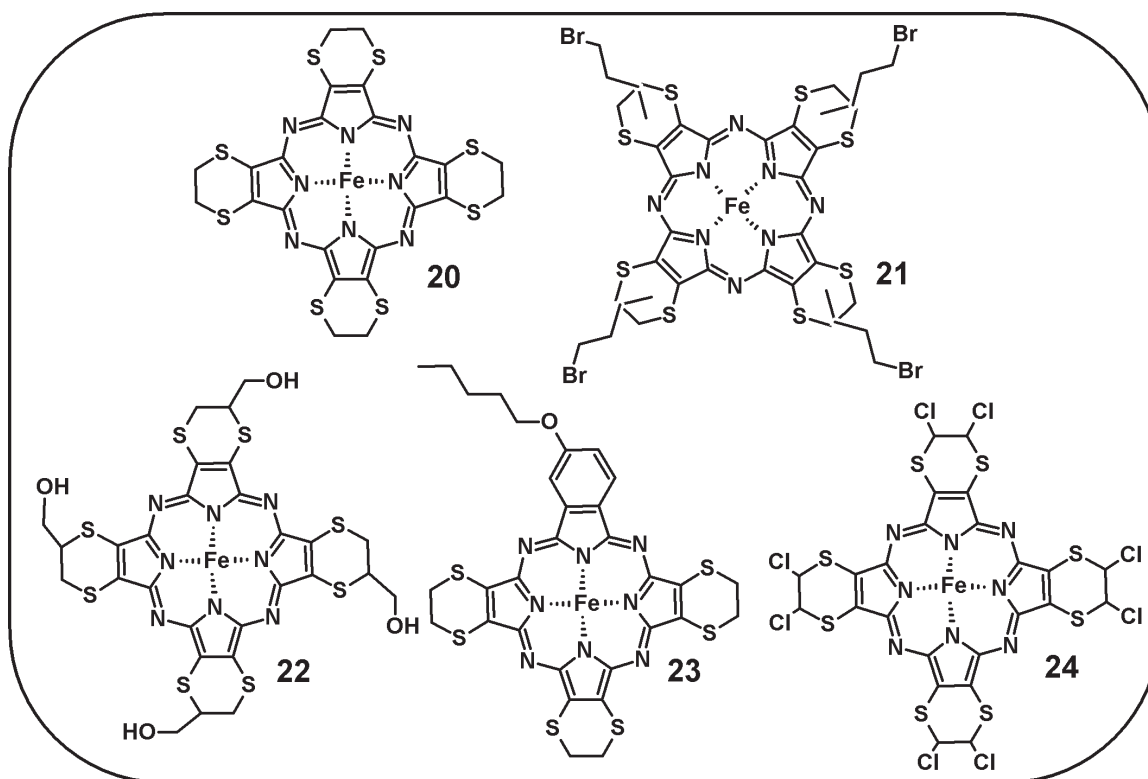

Figure 7. Chemical structure of iron(II) sulfanylporphyrazines **20–24**.

temperature. Lower catalytic ability was observed in the absence of light. It has been shown that the use of H_2O_2 as a source of oxygen resulted in the production of hydroxyl radicals as reactive oxygen species responsible for degradation of the substrate in the catalytic reaction. This process was called catalytic wet hydrogen peroxide oxidation (CWPO) and has potential for treatment of waste water [60]. As a result of research by Su et al. [61] and Theodoridis et al. [62], it was found that for the application of H_2O_2 as a commonly used oxygen atom donor in oxidation reactions catalyzed by iron(II) porphyrazine results in the hydroperoxo complex of iron(III) Pz formation. According to the reaction conditions there are two competitive redox routes: heterolysis (involving transfer of 2 electrons) and homolysis (1 electron transfer) leading to O–O bond cleavage (**Figure 8**). At acidic conditions, proton is utilized in heterolysis of O–O bond and transient high-valence iron-centered oxidizing species $Pz^{\bullet+}Fe^{IV}=O$ is generated as the reactive oxygen species (ROS). Of note is that the electronic structure of N4-ligand complexes allows for the stabilization of transient high-valent intermediates. For this reason, high-valence state iron species are often identified as ROS in biomimetic catalysis. On the other hand, homolysis of O–O bond in neutral and alkaline pH conditions leads to hydroxyl radical species formation as ROS, whereas the hydroperoxo complex of porphyrazine is transformed to porphyrazine radical $Fe^{III}=O^{\bullet}$ [61].

Another important objective for the application of iron phthalocyanines and porphyrazines as catalysts of the oxidation reactions of organic compounds is their use in chemical synthesis, which leads to new derivatives without using classical synthetic routes. The presence of Fe(II/III) tetraazaporphyrins with the use of suitable oxygen donors permits one or two electron oxidation reactions. As the result, various derivatives containing epoxy groups or hydroxyl, carbonyl and carboxyl substituents can be obtained. In the study aiming to assess catalytic properties of iron porphyrazines and phthalocyanines, cyclohexane was considered as a reference compound. In various studies, there were applied iron(II) phthalocyanine derivatives **25–27** and iron(III) phthalocyanine **28** as catalysts (**Figure 9**) and also diverse sources of oxygen: *tert*-butylhydroperoxide (TBHP), hydrogen peroxide, chloro-peroxybenzoic acid (m-CPBA), molecular oxygen and oxone. It was concluded that with an increase in temperature and catalyst concentration, an increase in reaction yield was observed. The source of
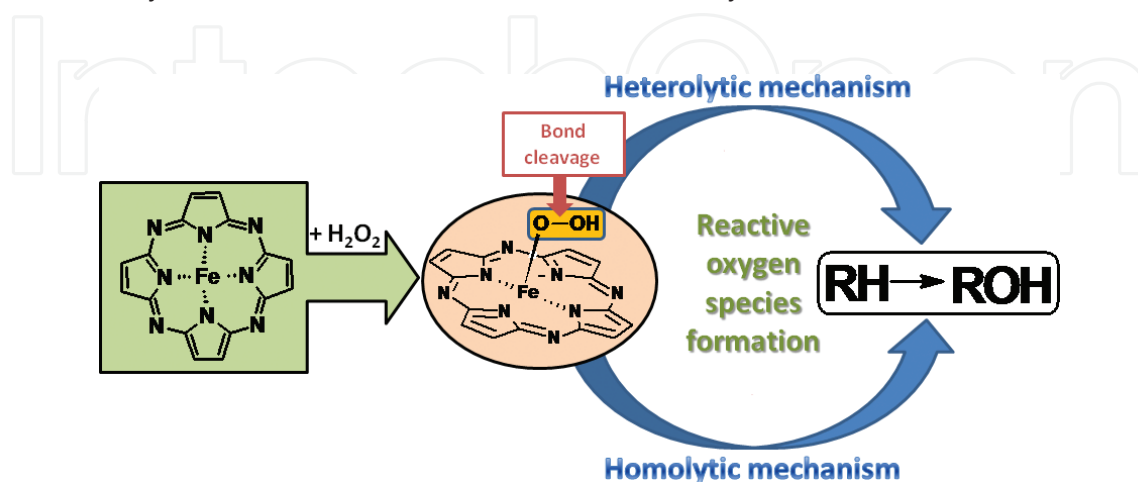

Figure 8. The heterolytic and homolytic mechanisms of O–O bond cleavage in the hydroperoxo complex of iron(III) porphyrazine following [61].
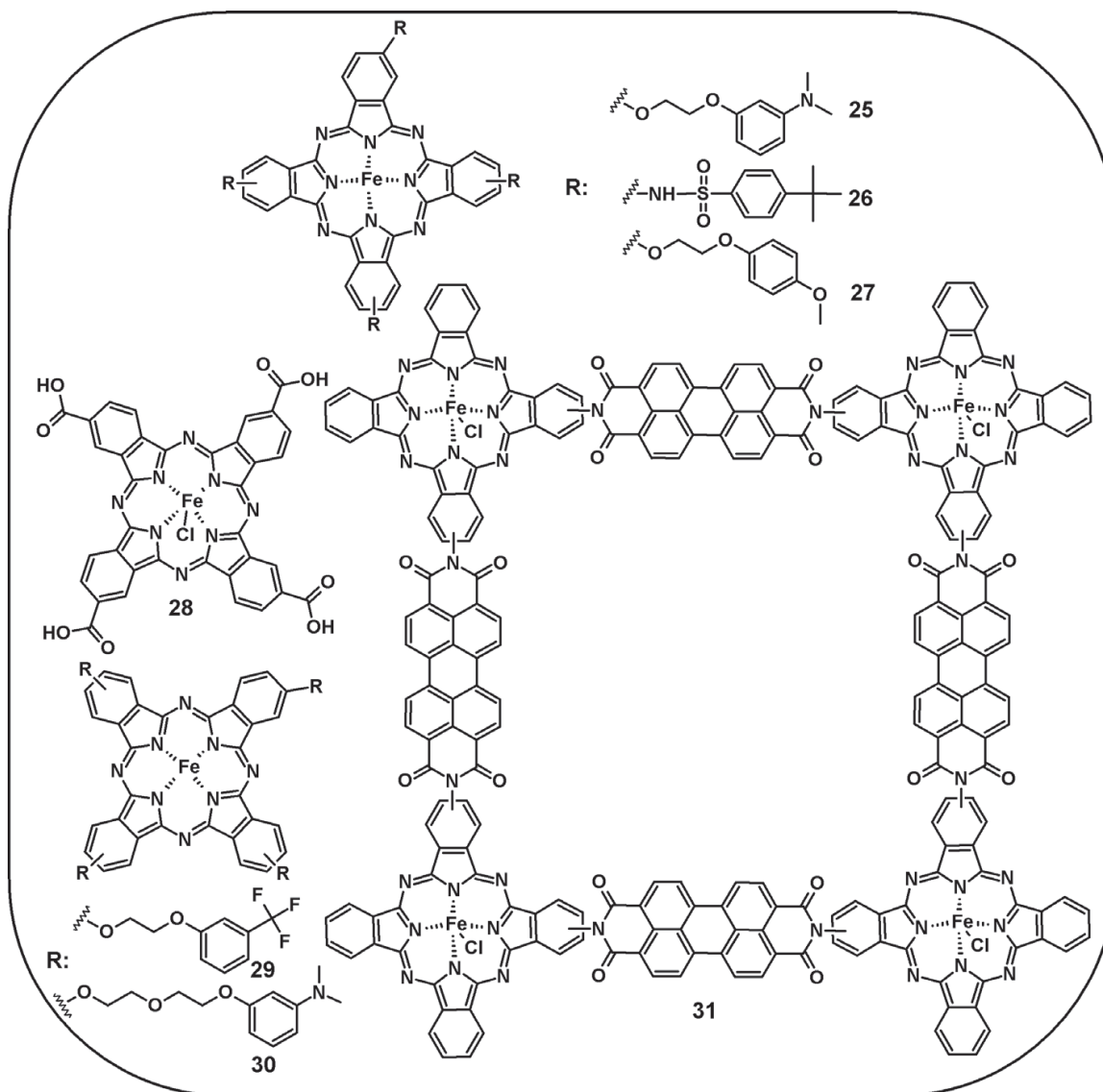
Figure 9. Structures of iron(II/III) phthalocyanine derivatives **25–30**, and cyclic tetramer **31**.

oxygen influenced the structures of obtained products. In all experiments monitored by the UV-Vis spectra, the degradation of the catalysts, manifested by a decrease of their Q-band absorption, was observed. However, in most cases, the catalytic processes proceeded, even after catalyst degradation, which can indicate the influence of other oxidation mechanisms, for example, Fenton reaction [63–66].

Lately performed study with iron(II) phthalocyanine, **29**, **30**, and the cyclic tetramer consisting of iron(III) phthalocyanine linked to 3,4,9,10-perylenetetracarboxylate, tentatively named FePPOP **31** (**Figure 9**) indicate the possibility to use these compounds toward catalytic oxidation reaction of benzyl alcohol. In the case of tetramer, it was found that **31** exhibited high stability and also exhibited the large turnover number of the reaction reaching the value of 960 [67–69]. However, in the initial phase of the experiment, the catalyst **31** acted much slower in comparison with the other compounds [69]. In addition, heterogeneous catalysts consisting

of unsubstituted iron(II) phthalocyanines deposited on the electrodes by electropolymerization were applied in oxidation reactions of organic compounds. Such reactions were carried out in two kinds of systems: (i) phenolic resin/unsubstituted iron(II) phthalocyanine or (ii) the phenolic resin/structurally branched iron(II) phthalocyanine [70, 71]. In another study, various thiol derivatives (e.g., 2-mercaptoethanol) were applied as substrates in electrooxidation reaction toward disulfides. Transparent indium tin oxide electrodes were modified with iron(II) tetraaminophthalocyanine [72, 73].

4. Summary

The iron(II/III) porphyrazines and phthalocyanines have interesting electrochemical properties, which were demonstrated in many valuable studies performed during the last 30 years. Moreover, many applications of these macrocycles were presented in medicine, in biomedical and analytical fields, in materials chemistry as well as in chemical synthesis. It clarifies why catalytic abilities of iron(II/III) tetraazaporphyrins became an object of intense studies. This chapter aimed to summarize the influence of peripheral substituents of iron(II/III) porphyrazines and phthalocyanines on their spectral and electrochemical properties. Electrochemical properties of iron(II/III) porphyrazine and phthalocyanine complexes are significantly influenced by the periphery of the macrocycle, which can lead to an increase or a decrease of their electrochemical activity. Similarly, an axial coordination of molecules to the central metal ion causes a shift of the oxidation potential of the macrocycle or splits peaks belonging to oxidation processes. Selected studies on iron(II/III) porphyrazines and phthalocyanines were found not only to present their interesting physicochemical features but also further perspective applications, and thus, they were discussed in more detail. What is of immense value for further applications of these molecules in materials chemistry and nanotechnology is that some macrocycles demonstrated an ability to form coordination assemblies alone or with nanostructures, including fullerenes, and molecular wires. Especially interesting are binuclear complexes based on iron(II/III) porphyrazine and phthalocyanine bridged by oxygen, nitrogen or carbon atoms. Interesting modification of classical redox processes was observed in novel potential molecular quantum-dot cellular automata cells in which phthalocyanines were connected "side-by-side" or by forming ball-type dimers in which there were utilized sophisticated linkers binding two phthalocyanine units at two sides rigidly with four linking arms. Porphyrinoid catalysts also have the designation by biomimetic catalysts, this being because they are more effective in carrying out the oxidation reactions of organic compounds to other catalysts. It is related to the increased electron-donor effect of the ferric cation, which is conjugated to the π-electron system of the macrocyclic ring. The advantages of iron(II/III) porphyrazines and phthalocyanines as catalysts include high selectivity, mild and environmentally friendly reaction conditions and low energy consumption during catalysis. Studies of catalytic properties or iron(II/III) Pzs and Pcs concerned mostly with their potential applications in oxidation reactions of linear and cyclic alkenes as well as photocatalytic degradation of organic dyes. Some studies assessed the ability of iron(II/III) tetraazaporphyrins and their dimers in decomposition and removal of organic pollutants from industrial wastes. A huge

area for further application of these macrocycles results from the electrochemical studies in which iron Pzs and Pcs were deposited on the surface of electrodes and further applied as selective anions sensors. To sum up, iron(II/III) tetraazaporphyrins appear to present many interesting perspectives for biomedical and technological applications.

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