Chapter 1

Free-Base and Metal Complexes of 5,10,15,20-Tetrakis(N-Methyl Pyridinium L)Porphyrin: Catalytic and Therapeutic Properties

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Abstract

Porphyrins are tetrapyrrole macrocycles that can coordinate transition metal ions such as iron, cobalt and magnesium and are able to perform a diversity of functions and applications. In biological systems, these molecules are associated with proteins involved in photosynthesis, cell respiration, cell death, antioxidant defence, among others. The stability and versatile applications of porphyrins inspired the synthesis of derivatives including 5,10,15,20-tetrakis(N-methyl pyridinium-4-yl)porphyrin (TMPyP) that is the object of the present chapter. In synthetic porphyrins such as TMPyP, the catalytic and photochemical properties can be achieved by the coordination with a diversity of central metal ions. In photodynamic therapy (PDT), TMPyP and other porphyrins act as photosensitizers. The photochemical properties of TMPyP and other porphyrins are also useful for the fabrication of solar cells. The catalytic properties require the presence of a central metal. The MnTMPyP have antioxidant activity that is influenced the capacity of membrane binding, substituents, and meso substituents. Manipulation of the interfacial confinement properties is one of the newest application areas of porphyrins. The association of porphyrins with different surfaces modulates the electronic and physicochemical properties of these molecules. All of these properties are the object of experimental and theoretical studies discussed in the present chapter.

Keywords: porphyrins, TMPyP, antioxidant activity, photodynamic therapy

1. Introduction

Porphyrins constitute a group of aromatic organic molecules, composed of four pyrrole rings linked by methene (═CH─) bridges (5, 10, 15 and 20), that are the *meso*-carbon atoms/positions [1]. Free base porphyrins are able to complex with metal ions such as iron, zinc, copper and others at themacrocycle center to form metalloporphyrins. Therefore, the properties of a porphyrin can be modulated by the inserting or changing the central metal and appending different substituents at the *peripheral* (β-positions (2, 3, 7, 8, 12, 13,17 and 18)) and *meso* positions (**Figure 1**). Furthermore, the activity of a metalloporphyrin frequently involves redox cycling of the central metal. When peripheral and meso substituents are exclusively hydrogen atoms, and two of the four macrocycle nitrogen atoms are protonated, this molecule is known as a free-base porphine. When different organic groups are appended at the *peripheral* or *meso* positions, these compounds are known as porphyrins [2]. The manipulation of different substituents and central metal provides a wide diversity of biochemical functions for porphyrins.

In biological systems, the porphyrins are associated with proteins involved in important cellular processes such as photosynthesis, molecular oxygen transport, cell respiration, cell death, the combat of the oxidative stress, biological synthesis, fat acid oxidation and others [1, 3–5]. The iron protoporphyrin IX (known as heme group) is the biological metalloporphyrin present in almost all biological processes. Heme is the prosthetic group of myoglobin, hemoglobin and a diversity of enzymes such as peroxidases, cytochromes, $NO^{\bullet}$ synthase and others. Besides iron ion, other metals are found in biological porphyrins, the magnesium ion in chlorophyll, and the cobalt ion in vitamin B 12 [6]. Biological and synthetic porphyrins and metalloporphyrins have been extensively investigated and applied in medicine, chemistry, sensing and other technological devices due to their catalytic, photochemical and photophysical properties [6, 7]. In biological systems, free-base porphyrins are largely used as photosensitizer (PS) in photodynamic therapy (PDT) [2, 5, 8, 9]. Otherwise, metalloporphyrins have been used for mimicking the function of hemeproteins such as cytochrome P-450 in oxidative catalysis and superoxide dismutase SOD against oxidative stress. Porphyrins are also used as building blocks and in transport chains of molecular devices [4, 9–11].

Porphyrins are versatile catalytic and therapeutic agents. The properties of porphyrins can be modulated by changing the central metal, substituents at the *peripheral* and *meso* positions and the microenvironment. Different microenvironments respond for the diversity of functions of heme group in the hemeproteins: oxygen transport, electron transport, hydroxylation, peroxide cleavage and others. The versatility of functions can also be achieved for synthetic porphyrins by manipulating their structures and microenvironments. One example of interchangeable functions of porphyrins is the substitution of the central metal in TMPyP (5,10,15,20-tetrakis(N-methyl pyridinium L)porphyrin). MnTMPyP exhibits antioxidant function, and it has been attributed to the superoxide dismutase (SOD)-like and

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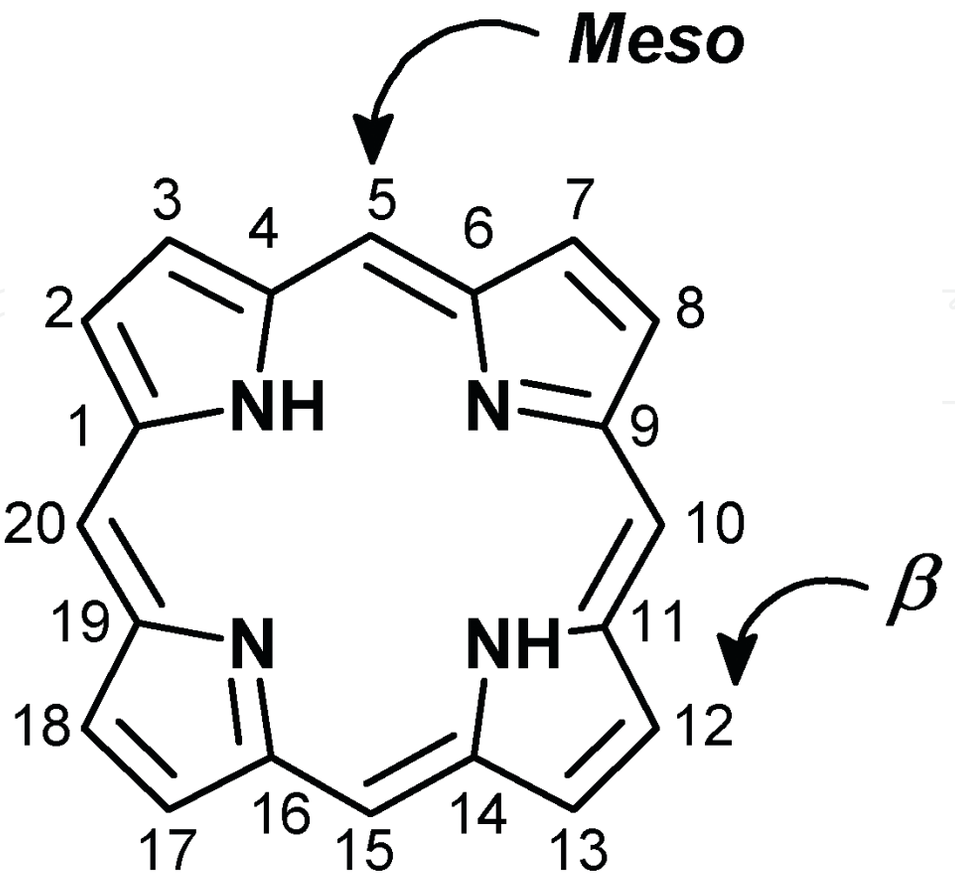

Figure 1. Free-base porphine with peripheral and meso positions.

glutathione peroxidase (GPx)-mimetic capacities [12, 13], while FeTMPyP exhibits pro-oxidant activity that responds to the toxicological effects of these compounds [14]. The pro-oxidant activity of FeTMPyP has been attributed to the generation of free radicals due to the homolytic cleavage of peroxides. The introduction and modification of substituents in a metalloporphyrin changes the redox potential and the solubility. In this regard, TMPyP and TPPS4 are examples of synthetic porphyrins made water soluble by the *meso* substitution of pyridine and sulfonate groups, respectively. Depending on the *meso* substituent, there is the possibility of a refined modulation of the porphyrin activity by isomerization. Previous studies comparing SOD activity of *ortho*, *meta* and *para* isomers of MnTMPyP (**Figure 2**) showed that the former exhibits the most effective SOD-like activity due to an appropriate combination of redox potential and electrostatic facilitation [15–18]. *Para* MnTMPyP exhibits a lower redox potential value that disfavors SOD activity [19]. However, the association of *para* MnTMPyP to negatively charged membranes (phosphatidylcholine (PC)/phosphatidylserine (PS)) modulates its redox potential toward a more efficient SOD activity [20]. Thus, the study of Araujo-Chaves et al. [13] is an example of the modulation of a porphyrin activity by the microenvironment. The different activities of TMPyP and other porphyrins are described herein.

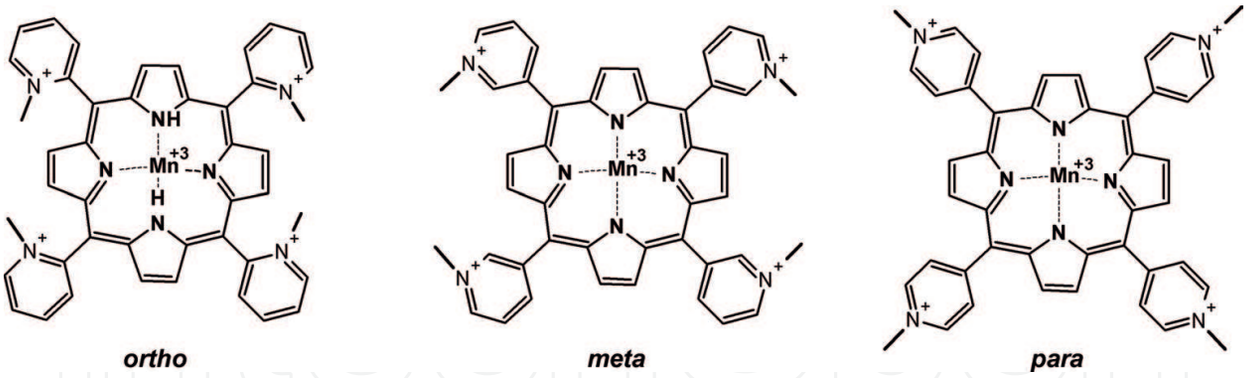

Figure 2. *Ortho, meta* and *para* isomers of MnTMPyP.

2. Biological applications of porphyrins

2.1. Porphyrins in photodynamic therapy (PDT)

2.1.1. A brief historical of PDT

The term PDT—photodynamic therapy—is recent. However, the heliotherapy—the therapeutic exposure to sunlight—was already used more than 4000 years ago by Egyptians, Greeks, and Indians as a treatment for several skin disorders, like psoriasis, vitiligo, cancer and even psychosis [21–29]. Heliotherapy, recently known as phototherapy, employs either UV and visible light with/without an exogenous photosensitizer. The photosensitizer is a molecule which when exposed to light absorbs determined wavelength becomes electronically excited and starts photochemical reactions that can produce a desirable beneficial effect, as in the case of vitamin D synthesis or damage and death, as in the case of tumor and infections treatment [2, 30]. Phototherapy without an exogenous photosensitizer is used in dermatology to treat vitiligo, eczema, neonatal jaundice and vitamin D deficiency, and even some cancer types [30–33]. During 18th and 19th centuries, phototherapy without exogenous photosensitizer was used in France in the treatment of many diseases, including tuberculosis, rheumatism, edema, rickets and paralysis [28, 34]. When an exogenous photosensitizer is used in tandem with the sunlight, this therapy is called photochemotherapy. An example of the exogenous photosensitizer is the psoralen series (**Figure 3**). These molecules are used as active treatments of HIV-associated dermatoses, seborrheic dermatitis, mycosis fungoids, prurigo, palmar and plantar pustulosis, among other diseases [30, 35]. The use of psoralens and ultraviolet light—UV (300–400 nm) was used by ancient Egyptians to treat vitiligo in the past and has been accepted for the treatment of psoriasis (PUVA) and in immunotherapy throughout the world [22, 27, 30, 35, 36].

Photodynamic therapy (PDT) is a non-invasive treatment method that uses light, photosensitizer and molecular oxygen for the treatments of cancer, inflammation, immunological

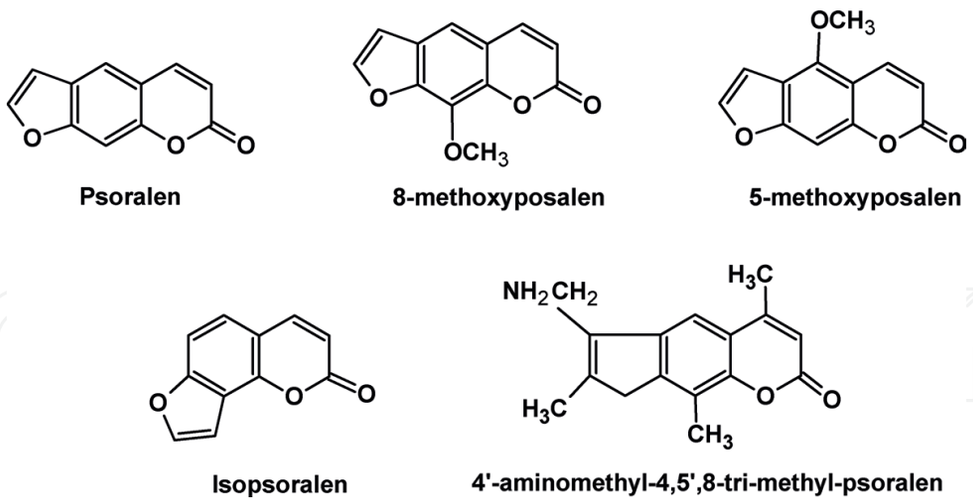

Figure 3. Psoralen series.

diseases and bacterial infections [8, 37–41]. In ancient times, phototherapy was used based on the observation of positive results without a mechanistic knowledge. People using and advocating phototherapy did know the key role of the photosensitizer in this type of treatment. In that times, the photosensitizer role was played by an endogenous biomolecule absorbing sunlight. The domain of the PDT mechanism initiated with the isolation of hematoporphyrin (Hp) (**Figure 4**) [28, 42]. From dried blood cells by Scherer in 1841 followed by the discovery of its fluorescence properties in 1871 [43]. In 1911 and 1913, the side effects of sun exposure after the administration of hematoporphyrin were described by Hausmann and Friedrich Meyer-Bertz. The latter scientist tested on himself the effect of Hp and sun and provided the first scientific communication of human photosensitization [44]. Besides, the powerful cytotoxic effect of phototherapy, another significant finding favoring the consolidation of this type of treatment, was the report of Auler and Banzer showing the affinity of Hp for cancer cells in 1942 [45]. In the following, several other studies led to the development of new range of porphyrinic photosensitizers [28, 43, 46–51].

2.1.2. The PDT mechanism

The Jablonski diagram [52], first proposed by Professor Alexander Jablonski in 1935, has been used to describe the photodynamic processes of photosensitizer molecules used in PDT. The PDT principles are based on the presence of an endogenous or exogenous photosensitizer in the target tissue that can absorb red light to be promoted to a long-lived electronic excited state. In the electronic excited state, the photosensitizer triggers photooxidative events directly or more commonly via energy transfer to molecular oxygen. The quantum yield triplet state generation depends on the molecular structure, and the energy transfer to molecular oxygen competes with other deactivating routes for the excited state [25].

According to **Figure 5**, Jablonski diagram shows that the ground state photosensitizer (S_0) can absorb a photon and be converted to the short-lived excited singlet state (S_n) at different

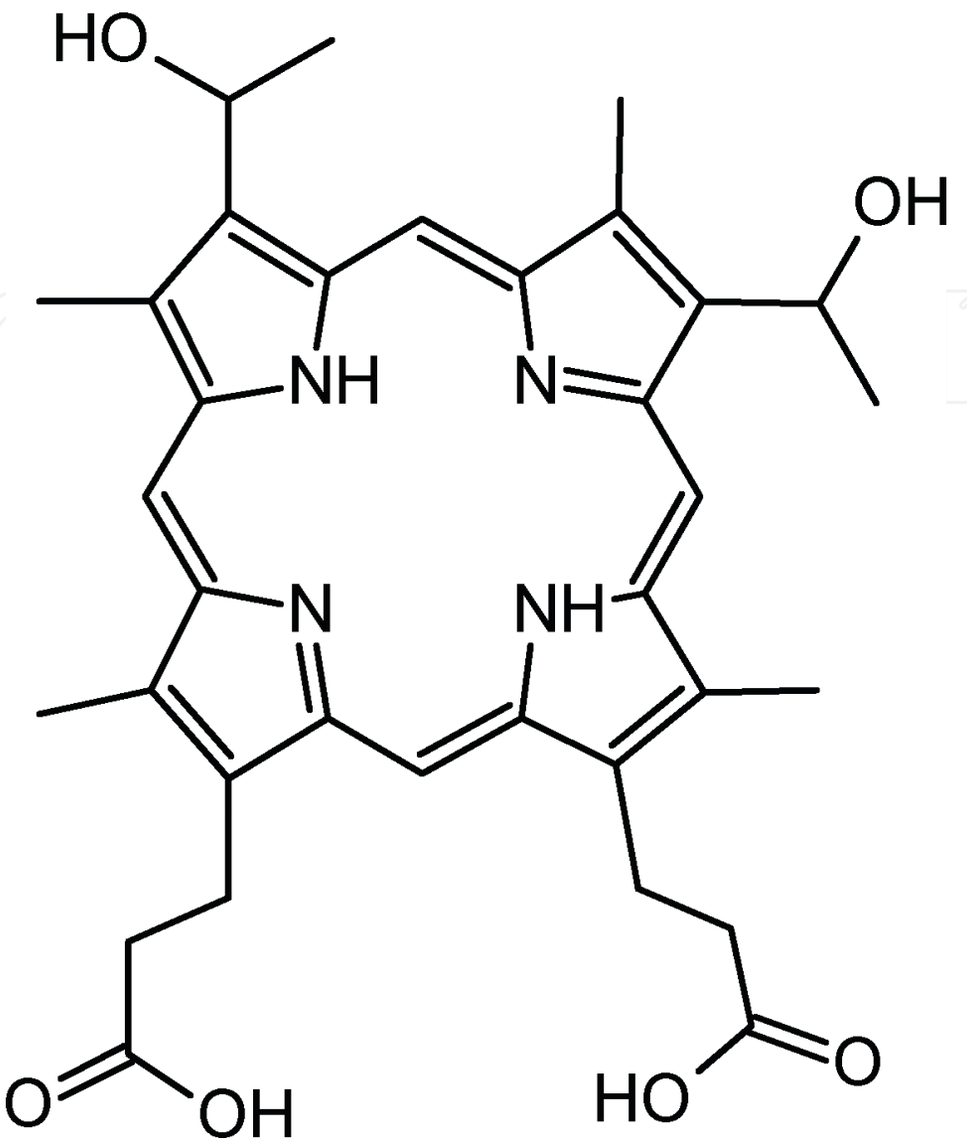

Figure 4. Hematoporphyrin.

vibrational sublevels (S_n'). The S_n state, if n > 1 can lose energy *via* internal conversion (IC) to populate the first excited single state (S_1). In the first singlet excited state, the photosensitizer can return to the ground state via fluorescence and thermal irradiation. Also, the S_1 state of the photosensitizer can undergo intersystem crossing by spin inversion and populate the lower-energy first excited triplet state (T_1), a long-lived state [2, 30, 37, 49]. At this point, two different reaction processes involving molecular oxygen can occur Type I or Type II processes. In the first process, Type I, the photosensitizer in a triplet excited state is reduced with organic substrates by electron exchange. The reduced photosensitizer can react with molecular oxygen ($^3O_2$) to produce reactive oxygen species (ROS) such superoxide anion ($O_2^{-\cdot}$), hydroxyl radical ($OH^{\cdot}$) and hydrogen peroxide (H_2O_2) [30, 37, 53]. In the second process, Type II, the triplet excited state photosensitizer transfers energy to molecular oxygen, resulting in a long-lived and highly reactive species, the singlet oxygen ($^1O_2$) [37, 49, 54]. Types I and II mechanisms occur concomitantly. However, Type II is the dominant process during PDT [30, 37].

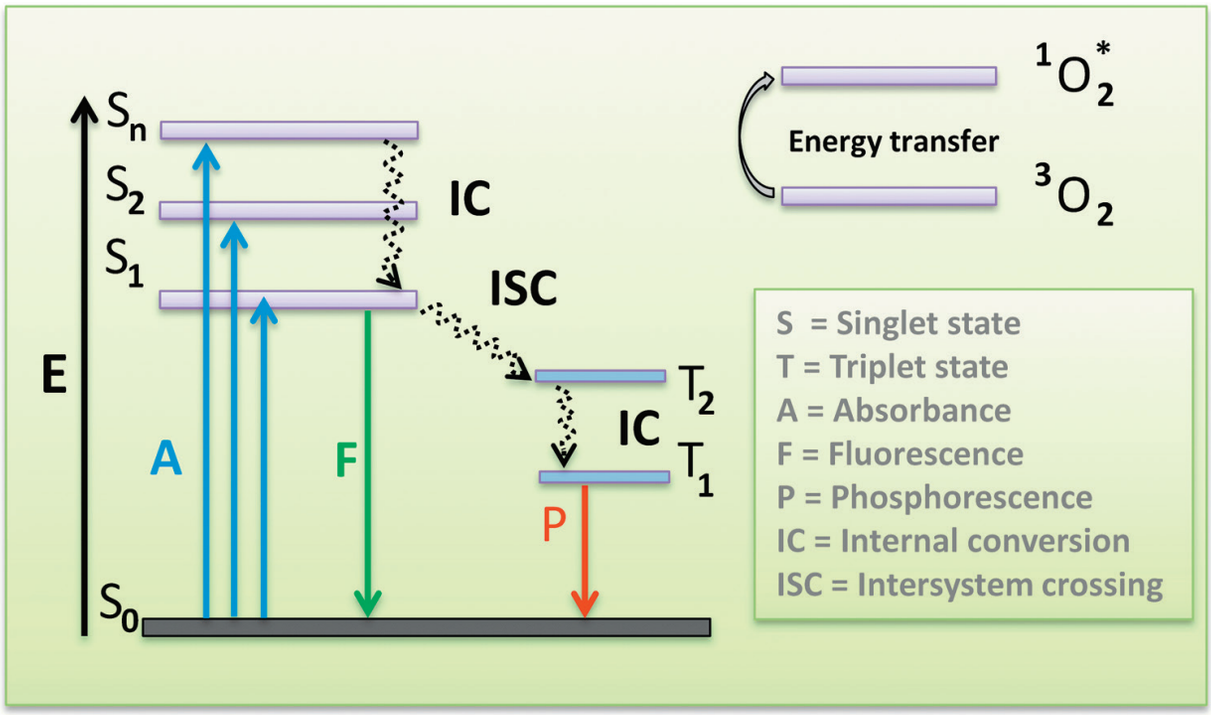

Figure 5. Energy levels of Jablonski diagram for a typical type II photosensitizer and oxygen.

In PDT, singlet oxygen is the principal reactive species. However, as well as others ROS, singlet oxygen has the capacity of damage limited due to its short lifetime (~100 ns in lipid regions of membranes and 250 ns in the cytoplasm) [30, 49, 55], and a diffusion range of approximately 45 nm in the cellular medium [28, 56–58]. The PDT has amino acid residues in proteins, unsaturated lipids, and DNA as the targets for oxidation leading to cell damage [59–61].

2.1.3. Porphyrin as photosensitizers

An ideal photosensitizer needs to have the following characteristics: (1) chemical purity; (2) high yield of singlet oxygen production; (3) high absorption coefficient in the red region of the visible spectrum (680–800 nm). Wavelengths longer than 900 nm should be avoided due to their insufficient energy to excite a dye photosensitizer to the triplet state; (4) efficient accumulation in tumor tissue associated with a rapid clearance in healthy organs; (5) low toxicity in the dark extensive to their metabolites; and (6) small aggregation [8, 30, 49, 62–64].

Porphyrins satisfy most of the desirable properties of photosensitizers, such as high efficiency of singlet oxygen generation, absorption of the higher wavelengths of the electromagnetic spectrum and a relatively higher affinity for malignant cells. Porphyrins have 18π electrons on the aromatic macrocycle that responds for the "*Soret*" band, with a strong absorption band around 400 nm, and Q bands in the 500–700 nm range that constitute the therapeutic window for this photosensitizer (**Figure 6**) [10, 65]. The absorption spectrum of the porphyrins is influenced by ligands and the central metal [66–68].

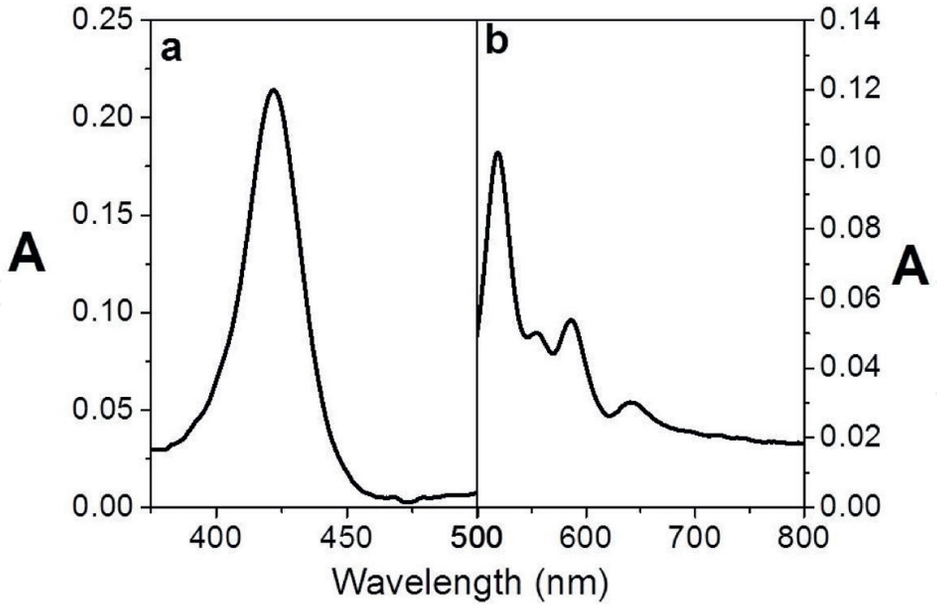

Figure 6. Porphyrin absorption spectrum. a = Soret band; b = Q band.

In the early twentieth century, data of literature described experiments that demonstrated the potential role of Hp in the detection and treatment of cancers; however, one of the major drawbacks was the large doses required to achieve consistent photosensitizer uptake in tumors, which led to inappropriate phototoxicity [45, 69–71]. In 1955, Schwartz et al. [72] demonstrated Hp to be impure and attributed selective fluorescence of malignant tissue after in vivo administration of Hp to a mixture of porphyrins with different properties. Subsequent studies led to the development of a derivative of hematoporphyrin (HpD) by the treatment of crude Hp with acetic and sulfuric acids, which enhanced tumor accumulation. The ability to accumulate selectively in neoplastic tissue using lower doses of HpD than Hp was reported by Lipson and coworkers [73–77]. In 1972, Diamond et al. demonstrated the destructive potential of HpD irradiated with white light on glioma in rats [78]. Six years later, Dougherty et al. reported the partial and complete response of many tumors, including malignant melanomas and carcinomas of the colon, breast, and prostate, treated by photodynamic therapy using HpD as a photosensitizer [79]. In the following, HpD compounds were purified, many of the less active monomers were removed, and the most efficient HpD derivatives were used to produce Photofrin (**Figure 7**).

For a complete study of different porphyrinic photosensitizers [80–109], it is recommended the reviews Josefsen et al. [2], Connor et al. [25], Pushpan et al. [28], and Ethirajan et al. [49]

Among a diversity of porphyrinic photosensitizers, *meso*-tetraphenylporphyrin (TPP) and TMPyP are readily synthesized and metallized, and several derivatives have been studied as a photosensitizer for PDT. The photochemical efficiency of anionic 5,10,15,20-*meso*-tetra(4-sulfonatophenyl)porphyrin (H_2TPPS_4) (**Figure 8A**) was compared with *meso*-tetraphenyl porphyrins with a lower number of sulfonate groups [99, 100] and

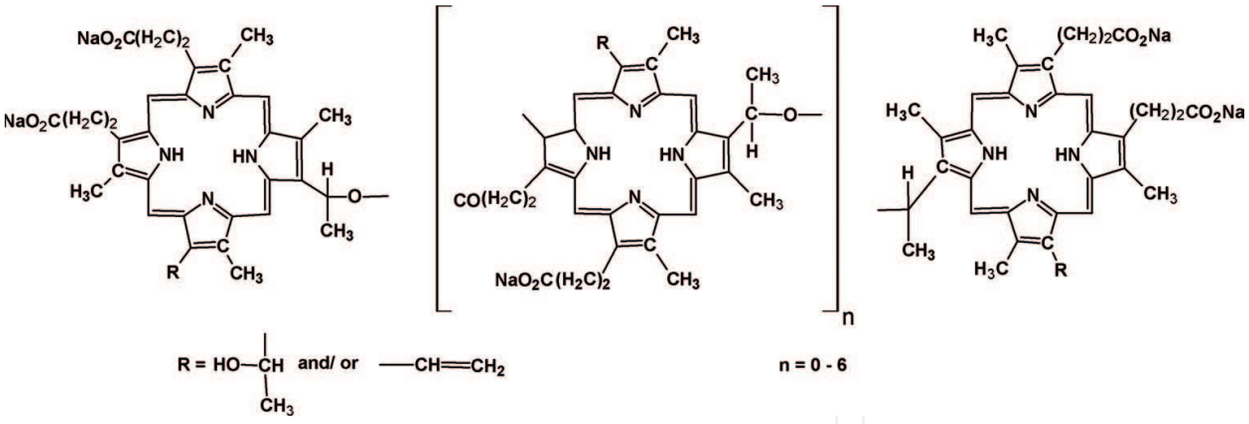

Figure 7. Photofrin.

with 5,10,15,20-tetrakis(4-sulfonatophenyl-21,23-dichalcogenaporphyrin [110] (**Figure 8B**). These studies showed that H_2TPPS_4 is less efficient in PDT than *meso*-tetraphenyl porphyrins with a lower number of sulfonate groups. Also, the replacement of nitrogen atoms of the macrocycle by chalcogens S and Se increased the photodynamic efficiency of the porphyrin in vitro and in vivo studies. Particularly in vivo, these chalcogen derivatives exhibited lower toxicity, morbidity and side effects post administration in animal models.

Regarding TMPyP, the focus of the present study, its efficiency as a photosensitizer is related to its topology. A study comparing photodamage in a mitochondrial membrane model modulated by the topology of TPPS4 and 5,10,15,20-tetrakis(N-methyl pyridinium L)porphyrin (TMPyP) [8] shows that in L-α-phosphatidylcholine/cardiolipin (PC/CL)liposomes (mitochondrial membrane model) both porphyrin can damage the membrane *via* the Type II mechanism. However, the injuries on the lipid membranes promoted by TMPyP were greater than the damages promoted by TPPS4 due to the affinity between TMPyP and this biological

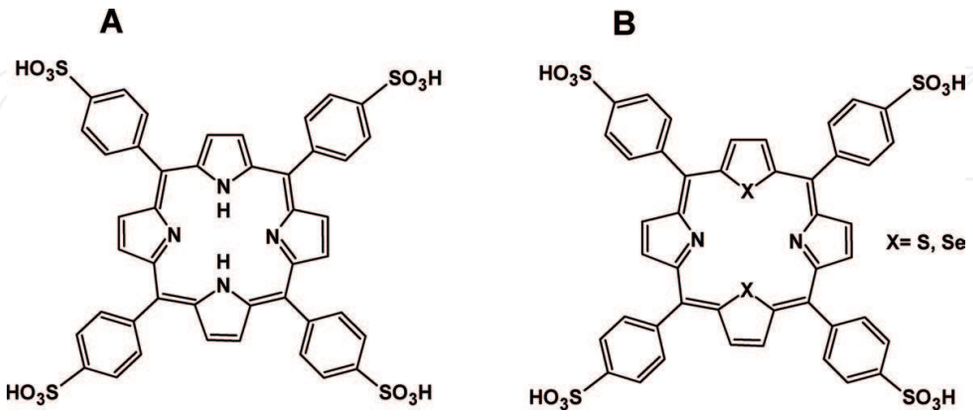

Figure 8. TPP-based photosensitizers. (A) Tetrasulfonated *meso*-tetraphenyl porphyrin; (B) *meso*-tetrakis(4-sulfonatophenyl)-21,23-dichalcogenaporphyrin.

structure [111, 112] that in turn influences the photosensitizer and the generation of long-lived singlet oxygen. In cells, the positively charged TMPyP accumulates in the nucleus and mitochondria and could attack DNA, mitochondrial DNA and cardiolipin. The association of TMPyP with the inner mitochondrial membranes due to the affinity to cardiolipin favors the generation of singlet oxygen in situ with a high efficiency since its concentration is higher in the hydrophobic core of the lipid bilayers. Metalloporphyrins have also been studied as potential sensitizers for PDT. However, the results were less promising than those obtained with the free-base species [113, 114].

2.2. Porphyrins in chemical therapy

The synthetic analogs of porphyrins are widely used in therapy of diseases connected to oxidative stress processes. A quantitative structure-activity relationship (QSAR) studies have been performed to identify the optimal active molecule within a series of analog structure characteristics to diversify the biological action of the compound. The QSAR studies can correlate the physicochemical characteristics that affect the compound's activity in biological systems. These studies assumed that the binding affinity of the compound to the target receptor could determinate the biological activity [115]. The biological effects of two meso-tetrakis porphyrins, TPPS4 (anionic) and TMPyP (cationic) demonstrated that the cationic porphyrin has affinity to the inner mitochondrial membrane [99]. Therefore, in mitochondria, Mn^{3+}TMPyP has been used as an antioxidant against superoxide ions. The replacement of manganese by an iron ion in TMPyP makes this porphyrin a prooxidant agent [116]. Au-porphyrins have been reported as excellent antiproliferative agents, showing cytotoxic effects on cancer cells. Regarding to the mimetic SOD activity of porphyrins, the correlation between the metal-centered reduction potential and the catalytic rate constant for the $O_2^{\bullet-}$ dismutation was found for Fe and Mn porphyrins. The structure-activity relationships have been established over the years by the rate-limiting step of metal reduction of this class of compounds [117]. Modulation of SOD activity has been achieved by decreasing the electron density of the groups at the meso and β-pyrrile positions, thus increasing the Mn^{3+}/Mn^{2+} potential and facilitating its reduction [118–120]. Either the mimetic SOD activity can occur when the $O_2^{\bullet-}$ is directed to the catalytic site by the metal-centered positive charges via electrostatic facilitation [118, 119]. The manganese (III) 5,10,15,20-tetrakis(N-ethylpyridinium-2-yl) porphyrin (Mn^{3+}TE-2-PyP^{5+}, $E_{½}$ = +228 mV *vs* NHE, $\log_{kcat}$ = 7.76) and manganese (III) 5,10,15,20-tetrakis(N-n-hexylpyridinium-2-yl) porphyrin (MnTnHex-2-PyP^{5+}, $E_{½}$ = +314 mV *vs* NHE, $\log_{kcat}$ = 7.48), alkylated manganese (III) 5,10,15,20-tetrakis(2-pyridyl)porphyrin (MnT-2-Pyp^{+}), combined the thermodynamic and electrostatic optimizations and yielded compounds because they exhibit the $E_{½}$ close to the reduction potential of the SOD enzyme and are excellent mimetics of the SOD activity ($E_{½}$ ≅ +300 mV *vs* NHE, kcat ≅ 2 × 10^9 M^{-1} s^{-1}) [19, 117–122]. Recently, it has been reported that the para isomer ($E_{½}$ = +60 mV *vs* NHE) of Mn^{3+}TMPyP is less efficient as a SOD mimic relative than the *ortho* isomer ($E_{½}$ = +260 mV *vs* NHE) [12, 19, 123, 124].

In a cell redox balance, the association of Mn^{3+}TMPyP to membrane lipid bilayers can be intrinsically related to the redox potential of the Mn^{2+}/Mn^{3+} couple. In homogeneous systems, Batinić-Haberle et al. [19] had reported the effect of Mn^{3+}TMPyP in a CL-containing inner

mitochondrial membrane under pH 11 to 7.8 conditions. The potential values of Mn^{2+}/Mn^{3+} redox process were found to be $E_{1/2}$ =94 mV for *ortho* Mn^{3+}TMPyP and $E_{1/2}$ = 42 and 50 mV, respectively, for *meta* and *para* isomers. However, in a heterogeneous system, Araujo-Chaves et al. [20] have reported that the *para* isomer has the redox potential increased by the association with the negatively charged interface of lipid bilayers. Interestingly, the association of *para* Mn^{3+}TMPyP to PC/PS liposomes at physiological pH exhibited a redox potential of +110 mV *vs* NHE. The shift of the Mn^{2+}/Mn^{3+} $E_{1/2}$ value to a more positive value favors the SOD and peroxidase activities. Theoretical calculations corroborated with these results.

3. Technological applications

Porphyrins free base are extensively applied in solar cells and sensor due to their photophysical characteristics. The intense absorption bands covering a significant range of the visible region of the electromagnetic spectrum and due to the relatively low cost of these compounds as compared with inorganic semiconductors make these molecules appropriate for application in solar cells. These characteristics experimentally observed are consistent with the results obtained by density functional theory (DFT). Therefore, DFT/time-dependent (TD)DFT calculation is a useful strategy for the molecular design of porphyrins with the more appropriate characteristics for application is dye-sensitizer solar cells (DSSCs) [125–129]. As an example, Santhanamoorthi et al. [129] have presented the theoretical study of newly designed porphyrin dyes (1–5) for DSSC applications. In this study, the authors calculated seven different structures of porphyrins and found the best characteristics for use in solar cells for two calculated molecules that were named Dyes 2 and 4. Dyes 2 and 4 presented smaller HOMO-LUMO energy gaps and absorption in Q band significantly stronger. Equally, DFT/TDDFT can be used for conceiving porphyrin derivatives for a diversity of technological applications. Theoretical calculations allow the prediction of the best characteristics for porphyrins to be used in technological applications and optimize the subsequent efforts for the synthesis.

3.1. Porphyrins in solar cells

Solar energy is an important source of energy (~3×10^{24} J $year^{-1}$) that sustains the life on the Earth [130–132], and it can be an alternative to using fossil fuels due to be a clean, inexhaustible and sustainable source of energy [133–139]. The utilization of solar energy as solar fuel or electricity is fundamental for the maintenance of development and live on Earth and has attracted the attention of various members of the scientific community.

O'Regan and Grätzel [140] have discussed dye-sensitized solar cells (DSSC), a viable and promising technology which have low-cost production and high power conversion efficiency [141–148]. To build an efficient system of the solar cell is necessary [149–152] three components: (1) dye (light-absorber); (2) a hole transport agent; and (3) an electron-transport agent. **Figure 9** shows the schematic representation of components and representative operational principles of DSSC.

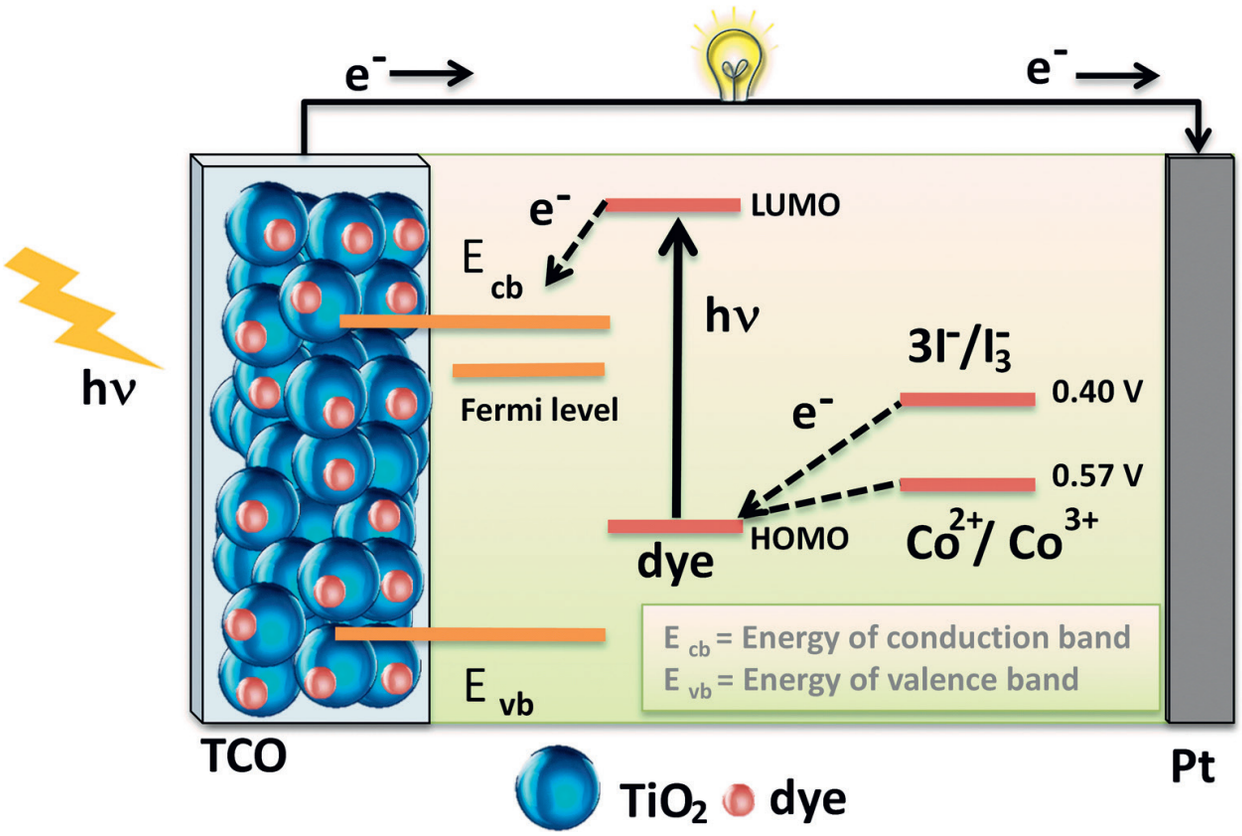

Figure 9. Schematic representation of components and representative operational principles of DSSC.

A typical DSSC device consists of a dye-sensitizer photoanode (TiO_2, anode) and a platinum counter electrode (Pt-coated, cathode) sandwiching an electrolyte that contains a redox mediator (iodine-based or cobalt complexes, redox mediator). Upon light illumination, the photoexcited dye in the LUMO level of sensitizer injects an electron into a conduction band (CB) of TiO_2, and then, the resultant oxidized dye is reduced by I^- species (or Co^{2+} complex). The injected electrons move through an external circuit to the platinized counter electrode. Finally, the I^- species (or Co^{2+} complex) is regenerated to produce the I_3^- species (or Co^{3+} complex) at the surface of the platinized counter electrode, and the circuit is completed [133]. The efficiency of conversion of light to electric power (η) increases when a light-absorbing the dye, and therefore, the choice of a suitable dye is essential to a high η [127, 144, 153–156].

Despite to the intense absorption band, typical porphyrins have poor light-harvesting ability in the Q bands, being necessary the introduction of a push-pull structure [157–160] and the elongation of porphyrin π-conjugated system into *meso* or β-positions to improve the light-harvesting property of porphyrins [158].

Porphyrin also can be used as a dye in thin layers on the porous TiO_2 film. However, this system results in weak absorption of irradiated light, being essential the development of a way to strongly absorb the light in the dye layer. Gold layer can have been used in these systems due

to its surface plasmon resonance (SPR) that offers an enhanced optical field with increased short-circuit current, which can be corroborated by theoretical calculations [161].

3.2. Porphyrins in catalysis and sensing

The application of metalloporphyrins in bioinorganic chemistry has attracted interest in catalytic reactions. Synthetic metalloporphyrins are mimetic models inspired two heme proteins: cytochrome P450 (biosynthesis and degradation of biomolecules) and peroxidases as lignin peroxidases (degrades the lignin-cell wall). In 1970, Groves et al. [162] designed the first-generation of metalloporphyrin chlorine (5,10,15,10-tetraphenyl-porphyrinato)iron(III), or [Fe^{3+}TPPCl], activated by iodosylbenzene (PhIO) revealed a catalytic activity in the epoxidation of alkenes and the hydroxylation of alkanes. About 30 years ago, Traylor and Tsuchyia [163] presented the first synthesis of porphyrins with more stability and more efficient catalytic activity due to the introduction of electronegativity and/or bulky auxiliaries groups such as halogen, nitro or sulfonate at the *meso* and/or β-pyrrolic positions, to obtain the second and third generation of porphyrin catalysts. Lately, the metal complexes like *meso*-tetrakis(penta fluorophenyl)porphyrin H_2(TPFPP) represent alternative possibilities to structural modification of porphyrins by nucleophilic substitution of its fluorine atoms [164, 165]. The second generation of porphyrins, especially the manganese (II) and iron(III) porphyrins is the most important representatives as catalysts in the epoxidation of alkenes (cyclohexane, adamantane, or n-hexane). In this case, during the epoxidation reactions, Mn and Fe ions can accept active species from different substrates and oxygen atom donors that result in metal-oxo species formation. In some conditions, the catalytic efficiency of iron(III) porphyrins can be limited due to the presence of some by-products resulted from the epoxidation of alkenes, for example to the allylic oxidation reactions. In anadamant oxidation reaction, the catalytic reaction of manganese porphyrins (MnPor) derived from 5,10,15,20-tetrakis(4-methoxyphenyl)porphyrin had an increased product yield of 1-adamantanol than those obtained with [Fe^{3+}TPPCl] catalyst [166]. The MnPors can exhibit different behaviors regarding the electron-withdrawing substituents in the macrocycle structure. Doro et al. [167] revealed that MnPors had lower catalysis efficient than the second generation of catalyst [Mn^{3+}PFTDCPP]Cl due the high-valence active species caused by the electronegativity of the substituents (fluoro and chlorine) at the *meso*-aryl positions of the macrocycle in [Mn^{3+}PFTDCPP]Cl. Consistently with this observation, Rayati et al. [168] made a comparative catalytic study of two partially brominated MnPs, namely [$Mn^{3+}Br_4$TPP]Cl and [$Mn^{3+}Br_4T_4$(-OME)PP]Cl revealing that the electron-deficient Mnps were a better catalyst than electron-rich MnPs. Lately, new materials of metalloporphyrin catalysts supported on mesoporous silica have shown a high efficiency of stability and reaction conditions. Poltowicz et al. [169] have studied the supported MnTMPyP catalysts on aluminated MCM-41 and SBA-15 mesoporous to investigate the oxidation of cyclooctane with molecular oxygen (as air) without the use of sacrificial co-reductant. Due to the existence diffusion limitations within the pore inner space, the supported MnTMPyP had increased the catalysis activity in the SBA-15 mesoporous because it exhibits increased-size pore. The catalytic activity of porphyrins, including TMPyP, allows the use of these compounds in sensing. Porphyrins can form complexes with almost all metals, and consequently, a broad diversity of catalytic properties

can be achieved. The central metal in porphyrins determines the affinity for additional ligands. In general, the complex of Cu^{2+} and Ni^{2+} has low affinity for additional ligands. The Mg^{3+}, Cd^{2+} and Zn^{2+} porphyrins form pentacoordinate complexes with square-pyramidal structure. The metalloporphyrins with (Fe^{2+}, Co^{2+}, Mn^{2+}) in the central position produce distorted octahedral structure with two axial ligands. Metallo *meso* tetrakis porphyrins have been extensively used in the voltammetric determination of oxygen, NO, sugars, organohalides, DNA, alcohols, dopamine and others. Therefore, due to their switchable structures and a diversity of catalytic properties, porphyrins are widely used in analytical chemistry. A diversity of porphyrins can be applied biosensors and as stationary phases in HPLC.

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References

[1] Battesby AR, Fookes CJR, Matcham GW, McDonald E. Biosynthesis of the pigments of life: formation of the macrocycle. Nature. 1980;**285**:4011–4022. DOI: 10.1038/285017a0

[2] Josefsen LB, Boyle RW. Unique diagnostic and therapeutic roles of porphyrins and phthalocyanines in photodynamic therapy, imaging and theranostics. Theranostics. 2012;**2**:916–966. DOI: 10.7150/thno.4571

[3] Mauzerall D. Porphyrins, Chlorophyll, and Photosynthesis. Vol. 5. Berlin, Heidelberg: Springer; 1977. pp. 117–124. DOI: 10.1007/978-3-642–66505-9_5

[4] Armstrong D. and Stratton R. D. Oxidative Stress and Antioxidant Protection: The Science of Free Radical Biology and Disease. Hoboken, New Jersey: John Wiley & Sons. 2016;**27**:415–470. DOI: 10.1002/9781118832431.

[5] Nantes IL, Crespilho FN, Mugnol KCU, Araujo-Chaves JC, Luz RAS, Nascimento OR, Pinto SMS. Magnetic Circular Dichroism Applied in the Study of Symmetry and Functional Properties of Porphyrinoids. David S. Rodgers. (Org.). Circular Dichroism: Theory and Spectroscopy. 1st ed. New York; Nova Science Publishers. 2010. pp. 321–344

[6] Van Santen R. Catalysis in perspective: Historic review. Beller M, Renken A, Van Santen R, editors. In Catalysis: From Principles to Applications. 1st ed. Weinheim, Germany; Wiley-VCH: 2012. pp. 3–19

[7] Latter MJ, Langford SJ. Porphyrinic molecular devices: Towards nanoscaled processes. International Journal of Molecular Sciences. 2010;**11**:1878–1887. DOI: 10.3390/ijms11041878.

[8] Kawai C, Araújo-Chaves JC, Magrini T, Sanches COCC, Pinto SMS, Martinho H, Daghastanli N, Nantes IL. Photodamage in a mitochondrial membrane model modulated by the topology of cationic and anionic meso-tetrakis porphyrin free bases. Photochemistry and Photobiology. 2014;**90**:596–608. DOI: 10.1111/php.12228

[9] Carvalho CMB, Brocksom TJ, Oliveira KT. Tetrabenzoporphyrins: Synthetic developments and applications. Chemical Society Reviews. 2013;**42**:3302–3317. DOI: 10.1039/C3CS35500D

[10] Robertson CA, Evans DH, Abrahamse H. Photodynamic therapy (PDT): A short review on cellular mechanisms and cancer research applications for PDT. Journal of Photochemistry and Photobiology B. 2009;**96**:1–8. DOI: 10.1016/j.jphotobiol.2009.04.001

[11] Bonnett R. Photosensitizers of the porphyrin and phthalocyanine series for photodynamic theory. Chemical Society Reviews. 1995;**24**:19–33. DOI: 10.1039/CS9952400019

[12] Ferrer-Sueta G, Vitturi D, Batinić -Harbele I, Fridovish I, Goldstein S, Czapski G, Radi R. Reactions of manganese porphyrins with peroxynitrite and carbonate radical anion. The Journal of Biological Chemistry. 2003;**278**:27432–27438. DOI: 10.1074/jbc.M213302200

[13] Araujo-Chaves JC, Yokomizo CH, Kawai C, Mugnol KCU, Prieto T, Nascimento OR, Nantes IL. Towards the mechanisms involved in the antioxidant action of MnIII [meso-tetrakis(4-N-methyl pyridinium) porphyrin] in mitochondria. Journal of Bioenergetics and Biomembranes. 2011;**43**:663–671. DOI: 10.1007/s10863-011-9382-3

[14] Pessoto FS, Inada NM, Nepomuceno MF, Ruggiero AC, Nascimento OR, Vercesi AE, Nantes IL. Biological effects of anionic meso-tetrakis (para-sulfonatophenyl) porphyrins modulated by the metal center. Studies in rat liver mitochondria. Chemico-biological Interactions. 2009;**181**:400–408. DOI: 10.1016/j.cbi.2009.07.012

[15] Richards RA, Hammos K, Joe M, Miskelly GM. Observation of a stable water-soluble lithium porphyrin. Inorganic Chemistry. 1996;**35**:1940–1944. DOI: 10.1021/ic941434w

[16] Tabata T, Andreo P, Shinoda K. An analytic formula for the extrapolated range of electrons in condensed materials. Nuclear Instruments and Methods in Physics Research Section B. 1996;**119**:461–470. DOI: 10.1016/S0168-583X(96)00687-8

[17] Tabata M, Nishimoto J, Ogata A, Kusano T, Nahar N. Metalation of water-soluble octabromoporphyrin with lithium(i), cadmium(II), and mercury(II). Bulletin of the Chemical Society of Japan. 1996;**96**(3):673–677. DOI: 10.1246/bcsj.69.673

[18] Batinić -Haberle I, Liochev SI, Spasojevic I, Fridovich I. A Potent superoxide dismutase mimis: manganese β-octabromo-meso-tetrakis-(N-methylpyridinium-4-yl)-porphyrin. Archives of Biochemistry and Biophysics. 1997;**343**:225–233. DOI: 10.1006/abbi.1997.0157

[19] Batinić -Haberle I, Benov L, Spasojevic I, Fridovich I. The ortho effect makes manganese (III) meso-tetrakis (N-methylpyridinium-2-yl) porphyrin a powerful and potentially useful superoxide dismutase mimic. The Journal of Biological Chemistry. 1998; **273**:24521–24528. DOI: 10.1074/jbc.273.38.24521

[20] Araujo-Chaves J, Kawai C, Melo AFAA, Mugnol KCU, Nascimento OR, Arantes JT, Crespilho FN, Nantes IL. Interaction and reaction of the antioxidant MnIII [meso-tetrakis(4-Nmethyi pyridinium) porphyrin] with the apoptosis reporter lipid phosphatidylserine. Current Physical Chemistry. 2013;**3**(2):187–198. DOI: 10.2174/1877946811303020009

[21] Edelson MF. Light-activated drugs. Scientific American. 1988;**259**:68–75

[22] Sternberg ED, Dolphin D. Porphyrin-based photosensitizers for use in photodynamic therapy. Tetrahedron. 1998;**54**:4151–4202. DOI: 10.1016/S0040–4020(98)00015-5

[23] Nayak CS. Photodynamic therapy in dermatology. Indian Journal of Dermatology, Venereology and Leprology. 2005;**71**:155–160. DOI: 10.4103/0378-6323.16228

[24] Pervaiz S, Olivo M. Art and science of photodynamic therapy. Clinical and Experimental Pharmacology and Physiology. 2006;**33**:551–556. DOI: 10.1111/j.1440-1681.2006.04406.x

[25] O'Connor AE, Gallagher WM, Byrne AT. Porphyrin and Nonporphyrin photosensitizers in oncology: preclinical and clinical advances in photodynamic therapy. Photochemistry and Photobiology. 2009;**85**:1053–1074. DOI: 10.1111/j.1751-1097.2009.00585.x

[26] Spikes JD. The historical development of ideas on applications of photosensitized reactions in health sciences. In: Bergasson RV, JoriG, Land EJ, Truscott TG, editors. In Primary Photo Processes in Biology and Medicine. New York; Plenum Press: 1985. pp. 209–227

[27] Epstein JM. Phototherapy and photochemotherapy. The New England Journal of Medicine. 1990;**32**:1149–1151. DOI: 10.1056/NEJM199004193221609

[28] Pushpan SK, Venkatraman S, Anand VG, Sankar J, Parmeswaran D, Ganesan S, Chandrashekar TK. Porphyrins in photodynamic therapy—a search for ideal photosensitizers. Current Medicinal Chemistry—Anti-Cancer Agents. 2002;**2**:187–207. DOI: 10.2174/1568011023354137

[29] Roelandts R. The history of phototherapy: Something new under the sun?. Journal of the American Academy of Dermatology. 2002;**46**:926–930. DOI: 10.1067/mjd.2002.121354

[30] Ormond AB, Freeman HS. Dye sensitizers for photodynamic therapy. Material. 2013;**6**:817–840. DOI: 10.3390/ma6030817.817-840

[31] Bonnett R. Photosensitizers of the porphyrin and phthalocyanine series for photodynamic therapy. Chemical Society Reviews. 1995;**24**:19–33. DOI: 10.1039/CS9952400019

[32] Gambichler T, Breuckmann FBS, Altmeyer P, Kreuter A. Narrowband UVB phototherapy in skin conditions beyond psoriasis. Journal of the American Academy of Dermatology. 2005;**52**:660–670. DOI: 10.1016/j.jaad.2004.08.047

[33] Paus S, Schmidt-Hubsch T, Wullner U, Vogel A, Klockgether T, Abele M. Bright light therapy in Parkinson's disease: A pilot study. Movement Disorders. 2007;**22**:1495–1498. DOI: 10.1002/mds.21542

[34] Cauvin JF. Des bienfaits de I'insolation. (FThesis) Paris. 1815

[35] Ledo E, Ledo A. Phototherapy, photochemotherapy, and photodynamic therapy: Unapproved uses or indications. Clinics in Dermatology. 2000;**18**:77–86

[36] Schmitt IM, Chimenti S, Gasparro FPJ. Psoralen-protein photochemistry—a forgotten field. Photochemistry and Photobiology B. 1995;**27**:101–107. DOI: 10.1016/1011-1 344(94)07101-S

[37] Swavey S. and Tran M. Porphyrin and Phthalocyanine Photosensitizers as PDT Agents: A New Modality for the Treatment of Melanoma. Recent Advances in the Biology, Therapy and Management of Melanoma. Croatia InTech (Dr. Lester Davids (Ed.)). 2013:Cap.11:253–283. DOI: 10.5772/54940.

[38] Vzorov AN, Dixon DW, Trommel JS, Marzilli LG, Compans RW. Inactivation of human immunodefiency virus type i by porphyrins. Antimicrobial Agents and Chemotherapy. 2002;**46**:3917–3925. DOI: 10.1128/AAC.46.12.3917-3925.2002

[39] Mcmahon KS, Wieman TJ, Moore PH, Fingar VH. Effects of photodynamic therapy using mono-L-aspartyl chlorin e6 on vessel constriction, vessel leakage, and tumor response. Cancer Research. 1994;**15**:5374–5379

[40] Neurath RA, Strick N, Debinath AK. Structural requirements for and consequences of an antiviral porphyrin binding to the V3 loop of the human immunodeficiency virus (HIV- 1) envelope glycoprotein gp120. Journal of Molecular Recognition. 1995;**8**:345–357. DOI: 10.1002/jmr.300080604

[41] Bamfield P. Chromic Phenomena: Technological Applications of Colour Chemistry. Cambridge, UK: The Royal Society of Chemistry; 2001. DOI: 10.1039/9781849731034

[42] Scherer H. Chemical-physiological investigations. Annalen der Chemie und Pharmacie 1841;**40**:1–64

[43] Hoppe- Seyler F. Ueber die Chemische Zusammensetzung des Eiters. Medicinisch-Chemische Untersuchungen. 1871;**4**:486–501

[44] Meyer- Bertz F. Untersuchungen uber due bioloische (photodynamische) wirkung des hamatoporphyrins und anderer derivative des blut-und gallenfarbstoffs. Deutsches Archiv Für Klinische Medizi. 1913;**112**:476–503

[45] Auler H, Banzer G. Untersucheungen uber die rolle der porphyrine bei geschwulst-kranken menschen und tieren. Zeitschrift für Krebsforschung und klinische Onkologie. 1942;**53**:65–68

[46] Maganiello LOJ, Figge FH. Cancer detection and therapy II. Journal of Bulletin of the School of Medicine, University of Maryland. 1951;**36**:3–7

[47] Thudichum JL. Tenth Report of the Medical Officer of the Privy Council. London: H. M. Stationary Office; 1867

[48] Rabb O. Ueber die Wirkung fluorizierender Stoffe auf Infusorien. Zeitschrift Fur Biologie. 1900;**36**:524–546

[49] Ethirajan M, Chen y, Joshi P, Pandey RK. The role of porphyrin chemistry in tumor imaging and photodynamic therapy. The role of porphyrin chemistry in tumor imaging and photodynamic therapy. Chemical Society Reviews. 2011;**40**:340–362. DOI: 10.1039/B915149B

[50] von Tappeiner H, Jesionek H. Therapeutische versuche mit fluoreszierenden stoffen. Munch Med. Wochenschr. 1093;**47**:2042–2044

[51] von Tappeiner HA, Jodlbauer A. Die sensibilisierende Wirkung fluorescierender Substanzen. Gesammelte Untersuchungen über die photodynamische Erscheinung., Leipzig, Germany: F. C. W. Vogel; 1907

[52] Jabłoński A. Über den Mechanismus der Photolumineszenz von Farbstoffphosphoren. Zeitschrift für Physik A Hadrons and Nuclei. 1935;**94**:38–46. DOI: 10.1007/BF01330795

[53] Zimcik P, Miletin M. Photodynamic Therapy. In: Lang AR, editor. In Dyes and Pigments: New Research. New York, NY, USA: Nova Science Publishers; 2008. pp. 1–62

[54] Turro NJ. Modern Molecular Photochemistry. California: University Science Books; 1991. pp. 583–593

[55] Figge FHJ. The relationship of pyrrol compounds to carcinogenesis. In: Moulton FR, editor. In AAAS Research Conference on Cancer. 1945; pp. 117–128. DOI: 10.7326%2F0003-4819-27-1-143

[56] Ochsner M. Photophysical and photobiological processes in the photodynamic therapy of tumours. Journal of Photochemistry and Photobiology B: Biology. 1997;**39**:1–18. DOI: 10.1016/S1011-1344(96)07428-3

[57] Rosenthal L, Ben-Hur E. Role of oxygen in the phototoxicity of phthalocyanines. International Journal of Radiation Biology. 1995;**67**(1):85–91. DOI: 10.1080/09553009514550111

[58] Moan JJ. On the diffusion length of singlet oxygen in cells and tissues. Photochemistry and Photobiology B. 1990;**6**:343–347. DOI: 10.1016/1011-1344(90)85104-5

[59] Zamzami N, Susin SA, Marchetti P, Hirsch T, Gomez-Monterrey I, Castedo M, Kroemer G. Mitochondrial control of nuclear apoptosis. The Journal of Experimental Medicine. 1996;**183**(4):1533–1544. DOI: 10.1084/jem.183.4.1533

[60] Gomer CJ, Luna M, Ferraio A, Wong S, Fischer AMR. Photodynamic therapy-mediated oxidative stress can induce expression of heat shock proteins. Cancer Research. 1996;**56**:2355–2360

[61] Hamblin M, Newman ELJ. Photosensitizer targeting in photodynamic therapy II. Conjugates of haematoporphyrin with serum lipoproteins. Journal of Photochemistry and Photobiology B. 1994;**26**:147–157. DOI: 10.1016/1011-1344(94)07036-9

[62] Ravanat JL, Di Mascio P, Martinez GR, Medeiros MHG, Cadet J. Singlet oxygen induces oxidation of cellular DNA. The Journal of Biological Chemistry. 2000;**275**:40601–40604. DOI: 10.1074/jbc.M006681200

[63] Castano AP, Demidova TN, Hamblin MR. Mechanisms in photodynamic therapy: part one-photosensitizers, photochemistry and cellular localization. Photodiagnosis and Photodynamic Therapy. 2004;**1**:279–293. DOI: 10.1016/S1572-1000(05)00007-4

[64] Dolmans DE, Fukumura D, Jain RK. Photodynamic therapy for cancer. Nature Reviews Cancer. 2003;**3**:380–387. DOI: 10.1038/nrc1071

[65] Carvalho CBM, Brocksom TJ, Oliveira KT. Tetrabenzoporphyrins: Synthetic developments and applications. Chemical Society Reviews. 2013;**42**:3302–3317. DOI: 10.1039/c3cs35500d

[66] Oleinick NL, Evans HH. The photobiology of photodynamic therapy: Cellular targets and mechanisms. Radiation Research. 1998;**150**:S146–S156. DOI: 10.2307/3579816

[67] Ben-Dror S, Bronshtein I, Wiehe A, Röder B, Senge MO, Erenberg B. On the correlation between hydrophobicity, liposome binding and cellular uptake of porphyrin sensitizers. Photochemistry and Photobiology. 2006;**82**:695–701. DOI: 10.1562/2005-09-01-RA-669

[68] Berg K, Bommer JC, Moan J. Evaluation of sulfonated aluminum phthalocyanines for use in photochemotherapy—cellular uptake studies. Cancer Letters. 1989;**44**:7–15. DOI: 10.1016/0304-835(89)90101-8

[69] Figge FH, Weiland GS, Manganiello LO. Cancer detection and therapy; affinity of neoplastic, embryonic, and traumatized tissues for porphyrins and metalloporphyrins. Proceedings of the Society for Experimental Biology and Medicine. 1948;**68**(3):640–641. DOI: 10.3181/00379727-68-16580

[70] Peck GC, Mack HP, Holbrook WA. Use of hematoporphyrin fluorescence in biliary and cancer surgery. Annals of Surgery. 1955;**21**:181–188

[71] Rassmussan-Taxdal DS, Ward GE, Figge FH. Fluorescence of human lymphatic and cancer tissues following high doses of intravenous hematoporphyrin. Fluorescence of human lymphatic and cancer tissues following high doses of intravenous hematoporphyrin. Journal of Cancer. 1955;**5**:619–624. DOI: 10.1002/1097-0142(1955)8:1<78::AID-CNCR2820080109>3.0.CO;2-L

[72] Schwartz SK, Absolon K, Vermund H. Some relationships of porphyrins, X-rays and tumours. University of Minnesota Medical Bulletin. 1955;**27**:7–8

[73] Lipson RL, Baldes EJ. The photodynamic properties of a particular hematoporphyrin derivative. Archives of Dermatology. 1960;**82**:208–516. DOI: 10.1001/archderm.1960.01580040026005

[74] Lipson RL, Baldes EJ, Gray MJ. Hematoporphyrin derivative for detection and management of cancer. Cancer. 1967;**20**:2255–2257. DOI: 10.1002/1097-0142(196712)20:12<2255::AID-CNCR2820201229>3.0.CO;2-U

[75] Lipson RL, Baldes EJ, Olsen AM. The use of a derivative of hematoporhyrin in tumor detection. Journal of the National Cancer Institute. 1961;**26**:1–11

[76] Lipson RL, Gray MJ, Blades E. Haematoporphyrin derivative for detection and management of cancer. Cancer. 1966;**20**:2255–2257. DOI: 10.1002/1097-0142(196712)20:12<2255::AID-CNCR2820201229>3.0.CO;2-U

[77] Gray MJ, Lipson RL, Maeck JVS, Parker L, Romeyn D. Use of hematoporphyrin derivative in detection and management of cervical cancer: A preliminary report. American Journal of Obstetrics & Gynecology. 1967;**99**:766–771. DOI: 10.1016/0002-9378(67)90392-4

[78] Diamond I, Granelli SG, McDonagh AF, Nielsen S, Wilson CB, Jaenicke R. Photodynamic therapy of malignant tumours. Lancet. 1972;**2**:1175–1177. DOI: 10.1016/S0140-6736(72)92596-2

[79] Dougherty TJ, Kaufman JE, Goldfarb A, WeishauptKR, Boyle D, Mittleman A. Photoradiation therapy for the treatment of malignant tumors. Cancer Research. 1978;**38**:2628–2635

[80] Usuda J, Kato H, Okunaka T, Furukawa K, Tsutsi H, Yamada K, Suga Y, Honda H, Nagatsuka Y, Ohira T, Tsuboi M, Hirano T. Photodynamic therapy (PDT) for lung cancers. Journal of Thoracic Oncology. 2006;**1**:489–493. DOI: 10.1016/S1556-0864(15)31616-6

[81] Sharman WM, Allen CM, van Lier JE. Photodynamic therapeutics: Basic principles and clinical applications. Drug Discovery Today. 1999;**4**:507–517. DOI: 10.1016/S1359-6446(99) 01412-9

[82] Dougherty TJ, Gomer CJ, Henderson BW, Jori G, Kessel D, Korbelik M, Moan J, Peng Q. Photodynamic therapy. Journal of the National Cancer Institute. 1998;**60**:889–905. DOI: 10.1093/jnci/90.12.889

[83] Silva JN, Filipe P, Morlière P, Mazière J-C, Freitas JP, Cirne de Castro JL, Santus R. Photodynamic therapies: Principles and present medical applications. Bio-Medical Materials and Engineering. 2006;**16**:S147–S154

[84] Allison RR, Mota HC, Sibata CH. Clinical PD/PDT in North America: An historical review. Photodiagnosis and Photodynamic Therapy. 2004;**1**:263–277. DOI: 10.1016/S1572-1000(04)00084-5

[85] Allison RR, Bagnato VS, Cuenca R, Downie GH, Sibata CH. The future of photodynamic therapy in oncology. Future Oncology. 2006;**2**:53–71. DOI: 10.2217/14796694.2.1.53

[86] Phillips D. Chemical mechanisms in photodynamic therapy with phthalocyanines. Progress in Reaction Kinetics and Mechanism. 1997;**22**:175–300

[87] Wohrle D, Hirth A, Bogdahn-Rai T, Schnurpfeil G, Shopova M. Photo-dynamic therapy of cancer: second and third generations of photosensitizers. Russian Chemical Bulletin. 1998;**47**:807–816. DOI: 10.1007/BF02498146

[88] Levy JG, Jones CA, Pilson LA. The preclinical and clinical development and potential application of benzoporphyrin derivative. International Photodynamic Therapy. 1994;**1**:3–5

[89] Aveline BM, Hasan T, Redmond RW. The effects of aggregation, protein binding and cellular incorporation on the photophysical properties of benzoporphyrin derivative monoacid ring A (BPDMA). Journal of Photochemistry and Photobiology B: Biology. 1995;**30**:161–169

[90] Stables GI, Ash DV. Photodynamic therapy. Cancer Treatment Reviews. 1995;**21**:311–323. DOI: 10.1016/0305-7372(95)90035-7

[91] Berdugo M, Bejjani RA, Valamanesh F, Savoldelli M, Jeanny JC, Blanc D, Ficheux H, Scherz A, Salomon Y, BenEzra D, Behar-Cohen F. Evaluation of the new photosensitizer stakel (WST-11) for photodynamic choroidal vessel occlusion in rabbit and rat eyes. Investigative Ophthalmology & Visual Science. 2008;**49**:1633–1644. DOI: 10.1167/iovs.07–0767

[92] Koudinova NV, Pinthus JH, Brandis A, Brenner O, Bendel P, Ramon J, Eshhar Z, ScherzA, Salomon Y. Photodynamic therapy with Pd-Bacteriopheophorbide (TOOKAD): Successful in vivo treatment of human prostatic small cell carcinoma xenografts. International Journal of Cancer. 2003;**104**:782–789. DOI: 10.1002/ijc.11002

[93] Trachtenberg J, Bogaards A, WeersinkRA, Haider MA, Evans A, McCluskey SA, Scherz A, Gertner MR, Yue C, Appu S, Aprikian A, Savard J, Wilson BC, Elhilali M. Vascular targeted photodynamic therapy with palladium-bacteriopheophorbide photosensitizer for recurrent prostate cancer following definitive radiation therapy: Assessment of safety and treatment response. Journal of Urology. 2007;**178**:1974–1979. DOI: 10.1016/j.juro.2007.07.036

[94] Trachtenberg J, Weersink RA, Davidson SR, Haider M. A, Bogaards A, Gertner MR, Evans A, Scherz A, Savard J, Chin JL, Wilson BC, Elhilali M. Vascular-targeted photodynamic therapy (padoporfin, WST09) for recurrent prostate cancer after failure of external beam radiotherapy: A study of escalating light doses. BJU International. 2008;**102**:556–562. DOI: 10.1111/j.1464-410×.2008.07753.x

[95] Razum NJ, Snyder AB, Doiron DR. SnET2: Clinical update. Proceedings of SPIE. 1996;**2675**:43–46. DOI: 10.1117/12.237549

[96] Selman SH, Keck RW. The effect of transurethral light on the canine prostate after sensitization with the photosensitizer tin (II) etiopurpurin dichloride: a pilot study. Journal of Urology. 1994;**152**:2129–2132

[97] MacDonald IJ, Dougherty TJ. Basic principles of photodynamic therapy. Journal of Porphyrins and Phthalocyanines. 2001;**5**:105–129. DOI: 10.1002/jpp.328

[98] Bonnett R, Martinez G. Photobleaching of photosensitisers used in photodynamic therapy. Tetrahedron. 2001;**57**:9513–9547. DOI: 10.1016/S0040-4020(01)00952-8

[99] Detty MR, Gibson SL, Wagner SJ. Current clinical and preclinical pho-tosensitizers for use in photodynamic therapy. Journal of Medicinal Chemistry. 2004;**47**:3897–3915. DOI: 10.1021/jm040074b

[100] Morgan AR, Garbo GM, Keck RW, Selman SH. New photosensitizers for photodynamic therapy: combined effect of metallopurpurin derivatives and light on transplantable bladder tumors. Cancer Research. 1998;**48**:194–198

[101] Ali H, van Lier JE. Metal complexes as photo- and radio-sensitizers. Chemical Reviews. 1999;**99**:2379–2450. DOI: 10.1021/cr980439y

[102] Mang TS, Allison R, Hewson G, Snider W, Moskowitz R. A phase II/III clinical study of tin ethyl etiopurpurin (Purlytin)-induced photodynamic therapy for the treatment of recurrent cutaneous metastatic breast cancer. The Cancer Journal From Scientific American. 1998;**4**:378–384

[103] Primbs GB, Casey R, Wamser K, Snyder WJ, Crean DH. Photodynamic therapy for corneal neovascularization. Ophthalmic Surgery, Lasers. 1998;**29**:832–838

[104] Kaplan MJ, Somers RG, Greenberg RH, Ackler J. Photodynamic therapy in the management of metastatic cutaneous adenocarcinomas: Case reports from phase 1/2 studies using tin ethyl etiopurpurin (SnET2). Journal of Surgical Oncology. 1998;**67**:121–125. DOI: 10.1002/(SICI)1096-9098(199802)67:2<121::AID-JSO9>3.0.CO;2-C

[105] Selman SH, Albrecht D, Keck RW, Brennan P, Kondo S. Studies of tin ethyl etiopurpurin photodynamic therapy of the canine prostate. Journal of Urology. 2001;**165**:1795–1801. DOI: 10.1016/S0022-5347(05)66416-6

[106] Rifkin R, Reed B, Hetzel F, Chen K. Photodynamic therapy using SnET2 for basal cell nevus syndrome: A case report. Clinical Therapeutics. 1997;**19**:639–641. DOI: 10.1016/S0149-2918(97)80089-6

[107] Hsi RA, Kapatkin A, Strandberg J, Zhu T, Vulcan T, Solonenko M, Rodriguez C, Chang J, Saunders M, Mason N, Hahn S. Photodynamic therapy in the canine prostate using motexafin lutetium. Clinical Cancer Research. 2001;**7**:651–660

[108] Kessel D, Thompson P, Saatio K, Nantwi KD. Tumor localization and photosensitization by sulfonated derivatives of tetraphenylporphine. Photochemistry and Photobiology. 1987;**45**:787–790. DOI: 10.1111/j.1751-1097.1987.tb07883.x

[109] Berg K, Western A, Bommer J, Moan J. Intracellular localization of sulfonated meso-tetraphenylporphines in a human carcinoma cell line. Photochemistry and Photobiology. 1990;**52**:481–487. DOI: 10.1111/j.1751-1097.1990.tb01789.x

[110] Stilts CE, Nelen MI, Hilmey DG, Davies SR, Gollnick SO, Oseroff AR, Gibson SL, Hilf R, Detty MR. Water-soluble, core-modified porphyrins as novel, longer-wavelength-absorbing sensitizers for photodynamic therapy. Journal of Medicinal Chemistry. 2000;**43**:2403–2410. DOI: 10.1021/jm000044i

[111] Nepomuceno MF, Tabak M, Vercesi AE. Opposite effects of Mn(III) and Fe(III) forms of meso-tetrakis(4-N-methyl pyridiniumyl) porphyrins on isolated rat liver mitochondria. Journal of Bioenergetics and Biomembranes. 2002;**34**:41–47. DOI: 10.1023/A:1013818719932

[112] Inada NM, da Silva AR, Jorge RA, BoreckyJ, Vercesi AE. Irradiated cationic meso-porphyrin rat liver mitochondria induces larger damage to isolated than the anionic form. Archives of Biochemistry and Biophysics. 2007;**457**:217–224. DOI: 10.1016/j.abb.2006.10.025

[113] Sommer S, Rimington C, Moan J. Formation of metal complexes of tumor-localizing porphyrins. FEBS Letters. 1984;**17**:267–271. DOI: 10.1016/0014–5793(84)81138-2

[114] Kennedy JC, Pottier RH. New trends in photobiology: Endogenous protoporphyrin IX, a clinically useful photosensitizer for photodynamic therapy. Journal of Photochemistry and Photobiology B. 1992;**6**:275–292. DOI: 10.1016/1011-1344(92)85108-7

[115] Henderson BW, Bellmier DA, Greco WR, Sharm A, Pandey RY, Vaughan LA, Weushauot KR, Dougherty TJ. An in vivo quantitative structure-activity relationships for a congeneric series of pyropheophorbide derivatives as photosensitizers for photsynamic therapy. Cancer Research. 1997;**57**:4000–4007

[116] Salvemini D, Riley DP, Cuzzocrea S. SOD mimetics are coming of age. Nature Reviews Drug Discovery. 2002;**1**:367–374. DOI: 10.1038/nrd796

[117] Rebouças JS, Spasojevic I, Batinić-Harbele I. Pure manganese (III) 5,10,15,20-tetrakis(4.bonzoic acid)porphyrin (MnTBAP) is not a superoxide dismutase mimic in aqueous systems: a case of structure-activity relationship as a watchdog mechanism in experimental therapeutics and biology. Journal of Biological Inorganic Chemistry. 2008;**13**(2):289–302. DOI: 10.1007/s00775-007-0324-9

[118] Vance CK, Miller AF. A simple proposal that can explain the inactivity of metal-substituted superoxide dismutases. Journal of the American Chemical Society. 1998;**120**(3):461–467. DOI: 10.1021/ja972060j

[119] Ellerby RM, Cabelli DE, Graden JA, Valentine JS. Copper-zinc superoxide dismutase: why not pH dependent. Journal of the American Chemical Society. 1996;**118**(28):6556–6561. DOI: 10.1021/ja953845x

[120] Goldstein S, Fridovich I, Czapski G. Kinetic properties of Cu, Zn-superoxide dismutase as a function of metal content—order restored. Free Radical Biology & Medicine. 2006;**41**(6):937–941. DOI: 10.1016/j.freeradbiomed/2006/05/026

[121] Saba H, Batinić -Harbele I, Munusamy S, Mitchell T, Lichti C, Megyesi J, MacMillan-Crow LA. Manganese porphyrin reduces renal injury and mitochondrial damage during ischemia/reperfusion. Free Radical Biology & Medicine. 2007;**42**(10):1571–1578. DOI: 10.1016/j.freeradbiomed.2007.02.016

[122] Zhao Y, Chaiswing L, Oberley TD, Batinić -Haberle I, St. Clair W, Epstein CJ, St. Clair D. A mechanism-based antioxidant approach for the reduction of skin carcinogenesis. Cancer Research. 2005;**65**(4):1401–1405. DOI: 10.1158/0008-5472.CAN-04-3334

[123] Haberle I, Rebouças JS, Spasojević I. Superoxide dismutase mimics: Chemistry, pharmacology, and therapeutic potential. Antioxidants & Redox Signaling. 2010;**13**(6):877–918. DOI: 10.1089/ars.2009.2876

[124] Nagami H, Umakoshi H, Shimanouchi T, Kuboi R. Variable SOD-like activity of liposome modified with Mn(II)–porphyrin derivative complex. Biochemical Engineering Journal. 2004;**21**(3):221–227. DOI: 10.1016/j.bej.2004.05.006

[125] Dong H, Zhou X, Jiang C. Molecular design and theoretical investigation on novel porphyrin derivatives for dye-sensitized solar cells. Theoretical Chemistry Accounts. 2012;**131**(2):1–11. DOI: 1007/s00214-012-1102-5

[126] Mugnol KCU, Martins MVA, Nascimento EC, Nascimento OR, Crespilho FN, Arantes JT, Nantes IL. Interaction of Fe^{3+}meso-tetrakis (2,6-dichloro-3-sulfonatophenyl)porphyrin with cationic bilayers: magnetic switching of the porphyrin and magnetic induction at the interface. Theorical Chemistry Accounts. 2011;**130**:829–837. DOI 10.1007/s00214-011-1055-0

[127] Nazeeruddin MK, De Angelis F, Fantacci S, Selloni A, Viscardi G, Liska P, Ito S, Bessho T, Gratzel M. Combined experimental and DFT-TDDFT computational study of photoelectrochemical cell ruthenium sensitizers. Journal of the American Chemical Society.2005;**127**(48):16835–16847. DOI: 10.1021/ja052467l

[128] Balanay MP, Kim DH. DFT/TD-DFT molecular design of porphyrin analogues for use in dye-sensitizer solar cells. Physical Chemistry Chemical Physics. 2008;**10**(33):5121–5127. DOI: 10.1039/b806097e

[129] Santhanamoorthi N, Lo C-M, Jiang J-C. Molecular design of porphyrins for dye-sensitized solar cells: a DFT/TDDFT study. The Journal of Physical Chemistry. 2013;**4**(3):524–530. DOI: 10.1021/jz302101j

[130] Grätzel M. Solar energy conversion by dye-sensitized photovoltaic cells. Inorganic Chemistry. 2005;**44**(20):6841–6851. DOI: 10.1021/ic0508371

[131] Grätzel M. Photoelectrochemical cells. Nature. 2001;**414**:338–344. DOI: 10.1038/35104607

[132] Araújo-Chaves JC, Tofanello A, Yokomizo CH, Carvalho-Jr WM, Souza FL, Nantes IL. Cytochrome c as an electron acceptor of nanostructured titania and hematite semiconductors. Journal of Energy Challenge and Mechanics. 2014;**1**:86–94

[133] Higashino T, Imahori H. Porphyrins as excellent dyes for dye-sensitized solar cells: recent developments and insights. Dalton Transactions. 2015;**44**(2):448–463. DOI: 10.1039/C4DT02756F

[134] Panda MK, Ladomenou K, Coutsolelos AA. Porphyrins in bio-inspired transformations: Light-harvesting to solar cell. Coordination Chemistry Reviews. 2012;**256**:2601–2627. DOI: 10.1016/j.ccr.2012.04.041

[135] Hoffert MI, Caldeira K, Benford G, Criswell DR, Green C, Herzog H, Jain AK, Kheshgi HS, Lackner KS, Lewis JS, Lightfoot HD, Manheimer W, Mankins JC, Mauel ME, Perkins LJ, Schlesinger ME, Volk TT, Wigley ML. Advanced technology paths to global climate stability: energy for a greenhouse planet. Science. 2002;**298**:981–987. DOI: 10.1126/science.1072357

[136] Blankenship RE, Tiede DM, Barber J, Brudvig GW, Fleming G, Ghirardi M, Gunner MR, Junge WD, Kramer M, Melis A, Moore TA, Moser CC, Nocera DG, Nozik AJ, Ort DR, Parson WW, Prince RC, Sayre RT. Comparing photosynthetic and photovoltaic efficiencies and recognizing the potential for improvementol. Science. 2011;**332**:805–809. DOI: 10.1126/science.1200165

[137] Grätzel M, Janssen RA, Mitzi JDB, Sargent EH. Materials interface engineering for solution-processed photovoltaics. Nature. 2012;**488**:304–312. DOI: 10.1038/nature11476

[138] Shih PM, Zarzycki J, Niyogi KK. Kerfeld CA. Introduction of a synthetic CO_2-fixing photorespiratory bypass into a cyanobacterium. The Journal of Biological Chemistry. 2014;**289**:9493–9500. DOI: 10.1074/jbc.C113.543132

[139] Falkowski PG, Raven JA. Aquatic Photosynthesis. Princeton: University Press; 2007

[140] O'Regan B, Grätzel M. A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO_2 films. Nature. 1991;**353**:737–740. DOI: 10.1038/353737a0

[141] Grätzel M. Recent advances in sensitized mesoscopic solar cells. Accounts of Chemical Research. 2009;**42**(11):1788–1798. DOI: 10.1021/ar900141y

[142] Knodler R, Sopka J, Harbach F, Grunling HW. Photoelectrochemical cells based on dye sensitized colloidal TiO_2 layers. Solar Energy Materials and Solar Cells. 1993;**30**(3):277–281. DOI: 10.1016/0927-0248(93)90147-U

[143] Hagfeldt A, Boschloo G, Sun L, Kloo L, Pettersson H. Dye-sensitized solar cells. Chemical Reviews. 2010;**110**(11):6595–6663. DOI: 10.1021/cr900356p

[144] Nazeeruddin MK, Kay A, Rodicio I, Humphry-Baker R, Mueller E, Liska P, Vlachopoulos N, Grätzel M. Conversion of light to electricity by cis-X2bis(2,2′-bipyridyl-4,4′-dicarboxylate)ruthenium(II) charge-transfer sensitizers (X = Cl-, Br-, I-, CN-, and SCN-) on nanocrystalline titanium dioxide electrodes. Journal of the American Chemical Society. 1993;**115**(14):6382–6390. DOI: 10.1021/ja00067a063

[145] Hagfeldt A, Grätzel M. Molecular photovoltaics. Journal of the American Chemical Society. 2000;**33**(5):269–277. DOI: 10.1021/ar980112j

[146] Grätzel M. Perspectives for dye-sensitized nanocrystalline solar cells. Progress in Photovoltaics. 2000;**8**(1):171–185. DOI: 10.1002/(SICI)1099-159X(200001/02)8:1<171::AID-PIP300>3.0.CO;2-U

[147] Gao F, Wang Y, Shi D, Zhang J, Wang M, Jing X, Humphry-Baker R, Wang P, Zakeeruddin SM, Grätzel M. Enhance the optical absorptivity of nanocrystalline TiO_2 film with high molar extinction coefficient ruthenium sensitizers for high performance dye-sensitized solar cells. Journal of the American Chemical Society. 2008;**130**(32):10720–10728. DOI: 10.1021/ja801942j

[148] Tan LL, Huang JF, Shen YL, Xiao M, Liu JM, Kuang DB, Su CY. Highly efficient and stable organic sensitizers with duplex starburst triphenylamine and carbazole donors for liquid and quasi-solid-state dye-sensitized solar cells. Journal of Materials Chemistry A. 2014;**2**:8988–8994

[149] Zhou H, Fan T, Zhang D. An insight into artificial leaves for sustainable energy inspired by natural photosynthesis. ChemCatChem. 2011;**3**(3):513–528. DOI: 10.1002/cctc.201000266

[150] Liu L-N, Duquesne K, Oesterhelt F, Sturgis JN, Scheuring S. Forces guiding assembly of light-harvesting complex 2 in native membranes. Proceedings of the National Academy of Sciences of the United States of America. 2011;**108**(23):9455–9459. DOI: 10.1073/pnas.1004205108

[151] Lott GA, Perdomo-Ortiz A, Utterback JK, Widom JR, Aspuru-Guzik A, Marcus AH. Conformation of self-assembled porphyrin dimers in liposome vesicles by phase-modulation 2D fluorescence spectroscopy. Proceedings of the National Academy of Sciences of the United States of America. 2011;**108**(40):16521–16526. DOI: 10.1073/pnas.1017308108

[152] Gust D, Moore TA, Moore AL. Realizing artificial photosynthesis. Faraday Discuss. 2012;**155**:9–26. DOI: 10.1039/C1FD00110H

[153] Péchy P, Renouard T, Zakeeruddin S, Humphry-Baker MR, Comte P, Liska P, Cevey L, Costa E, Shklover V, Spiccia L, Deacon GB, Bignozzi CA, Grätzel M. Engineering of efficient panchromatic sensitizers for nanocrystalline TiO_2-based solar cells. Journal of the American Chemical Society. 2001;**123**(8):1613–1624. DOI: 10.1021/ja003299u

[154] Zeng W, Cao Y, Bai Y, Wang Y, Shi Y, Zhang M, Wang F, Pan C, Wang P. Efficient dye-sensitized solar cells with an organic photosensitizer featuring orderly conjugated ethylenedioxythiophene and dithienosilole blocks. Chemistry of Materials. 2010;**22**(5):1915–1925. DOI: 10.1021/cm9036988

[155] Tsao HN, Burschka J, Yi C, Kessler F, Nazeeruddin MK, Grätzel M. Influence of the interfacial charge-transfer resistance at the counter electrode in dye-sensitized solar cells employing cobalt redox shuttles. Energy & Environmental Science. 2011;**4**(12):4921–4924. DOI: 10.1039/C1EE02389F

[156] Xu M, Zhang M, Pastore M, Li R, De Angelis F, Wang P. Joint electrical, photophysical and computational studies on D-π-A dye sensitized solar cells: The impacts of dithiophene rigidification. Chemical Science. 2012;**3**(4):976–983. DOI: 10.1039/C2SC00973K

[157] Yella A, Lee H-W, Tsao HN, Yi C, Chandiran AK, Nazeeruddin MK, Diau EWG, Yeh C-Y, Zakeeruddin SM, Grätzel M. Porphyrin-sensitized solar cells with cobalt (II/III)–based redox electrolyte exceed 12 percent efficiency. Science. 2011;**334**(6056):629–634. DOI: 10.1126/science.1209688

[158] Lu HP, Tsai CY, Yen WN, Hsieh CP, Lee CW, Yeh CY, Diau EWG. Control of dye aggregation and electron injection for highly efficient porphyrin sensitizers adsorbed on semiconductor films with varying ratios of coadsorbate. The Journal of Physical Chemistry C. 2009;**113**(49):20990–20997. DOI: 10.1021/jp908100v

[159] Lee CW, Lu HP, Lan CM, Huang YL, Liang YR, Yen WN, Liu YC, Lin YS, Diau EWG, Yeh CY. Novel zinc porphyrin sensitizers for dye-sensitized solar cells: synthesis and spectral, electrochemical, and photovoltaic properties. Chemistry - A European Journal. 2009;**15**(6):1403–1412. DOI: 10.1002/chem.200801572

[160] Hsieh C-P, Lu H-P, Chiu C-L, Lee C-W, Chuang S-H, Mai C-L, Yen W-N, Hsu S-J, Diau EW-G, Yeh C-Y. Synthesis and characterization of porphyrin sensitizers with various electron-donating substituents for highly efficient dye-sensitized solar cells. Journal of Materials Chemistry. 2010;**20**(6):1127–1134. DOI: 10.1039/B919645E

[161] Baba A, Wakatsuki K, Shinbo K, Kato K, Kaneko F. Increased short-circuit current in grating-coupled surface plasmon resonance field-enhanced dye-sensitized solar cells. Journal of Materials Chemistry. 2011;**21**(41):16436–16441. DOI: 10.1039/C1JM12935J

[162] Groves JT, Nemo TE, Myers RS. Hydroxylation and epoxidation catalyzed by iron-porphine complexes. Journal of the American Chemical Society. 1979;**101**(4):1032–1033. DOI: 10.1021/ja00498a040

[163] Traylor TG, Tsychyia S. Perhalogenated tetraphenylhemins: Stable catalysts of high turnover catalytic hydroxylations. Inorganic Chemistry. 1987;**26**:1338–1339. DOI: 10.1021/ic00255a028

[164] Silva S, Pereira PMR, Silva P, Paz FAA, Faustino MAF, Cavaleiro JAS, Tomé J. Porphyrin and phthalocyanine glycodendritic conjugates: synthesis, photophysical and photochemical properties. Chemical Communications. 2012;**48**(30):3608–3610. DOI: 10.1039/C2CC17561D

[165] Costa JIT, Tomé J, Cavaleiro J. 5,10,15,20 -Tetrakis(pentafluorophenyl)porphyrin: A versatile platform to novel porphyrinic materials. Porphyrins Phtalocyanines. 2011;**15**(11):1116. DOI: 10.1142/S1088424611004294

[166] Nakagaki S, Ferreira GKB, Ucoski GM, Castro KADF. Chemical reactions catalyzed by metalloporphyrin-based metal-organic frameworks. Molecules. 2013;**18**(6):7279–7308. DOI: 10.3390/molecules18067279

[167] Doro FG, Smith AG, Assis MD. Oxidation of alkanes and alkenes by iodosylbenzene and hydrogen peroxide catalysed by halogenated manganese porphyrins in homogeneous solution and covalently bound to silica. Journal of Molecular Catalysis A: Chemical. 2000;**164**:97–108. DOI: 10.1016/S1381–1169(00)00352-6

[168] Rayati S, Zavaki S, Valinejad H. Oxidation of hydrocarbons with tetra-n-butylammonium peroxy monosulfate catalyzed by β-tetrabromo-meso-tetrakis(4-methoxyphenyl)- and β -tetrabromo-meso-tetraphenylporphyrinatomanganese(III). Turkish Journal of Chemistry. 2014;**38**(4):611–616. DOI: 10.3906/kim-1310-35

[169] Poltowicz J, Pamin K, Matachowski L, Serwicka EM, Mokaya R, Xia Y, Olejniczak Z. Oxidation of cyclooctane over Mn(TMPyP) porphyrin-exchanged Al,Si-mesoporous molecular sieves of MCM-41 and SBA-15 type. Catalysis Today. 2006;**14**:287–292. DOI: 10.1016/j.cattod.2006.02.015