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# Technological Applications of Porphyrins and Related Compounds: Spintronics and Micro-/Nanomotors

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## Abstract

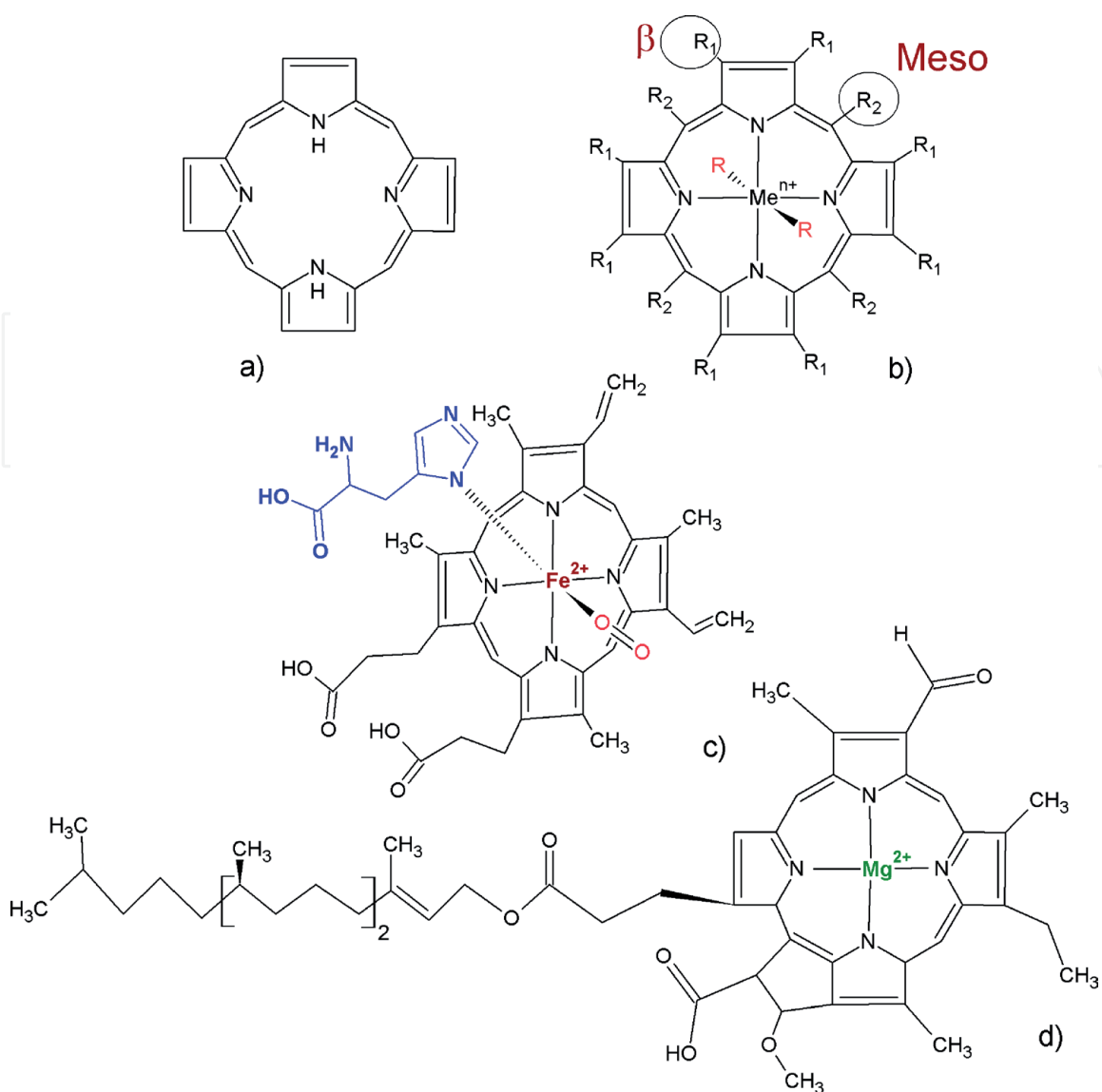
The vital role played by porphyrins in cells and their use in therapeutic processes are well known. More recently, the technological applications of porphyrins have attracted the attention of researchers. Porphyrins have the property of half-metallic material, i.e., molecules that can host transition metals making feasible the production of spin-polarized electronic states at different channels. Therefore, porphyrins and hemeproteins are among the materials that have spin-filtering property to be applied in spintronics. Molecular spintronics is an emerging and highly relevant field due to their applications to the development of high-capacity information-storage devices and quantum computers. The catalytic properties of porphyrins and related compounds such as the hemeproteins are also applicable in the fabrication of micro-/nanomotors (MNMs). In this chapter, we describe the advances and future perspectives in the technological applications of porphyrins and related compounds in spintronic devices and micro-/nanomotors.

**Keywords:** porphyrins, cytochrome *c*, peroxidases, interfaces, advanced materials, micro-/nanomotors, micro-/nanorobots, spintronics, semiconductors, nanotechnology

## 1. Introduction

### 1.1 Porphyrins and hemeproteins

Porphyrins are essential compounds for the metabolism of living organisms. Porphyrins result from the substitution of porphine, which is a macrocycle formed by four pyrrole rings linked via methine bridges (**Figure 1a**). The tetrapyrrole ring has space for the coordination of a central transition metal ion with the four nitrogen atoms of the pyrrole rings to form a metalloporphyrin (**Figure 1b**) [1]. The properties of porphyrins can be modulated by substitutions at the  $\beta$ - and *meso*-positions, the central transition metal ions, and the metal ion axial ligands (**Figure 1b**). Another modification of porphyrin ring is the insertion of a carbene in a free-base ring to form the N,N'-vinyl-bridged porphyrin and the insertion of a carbene into



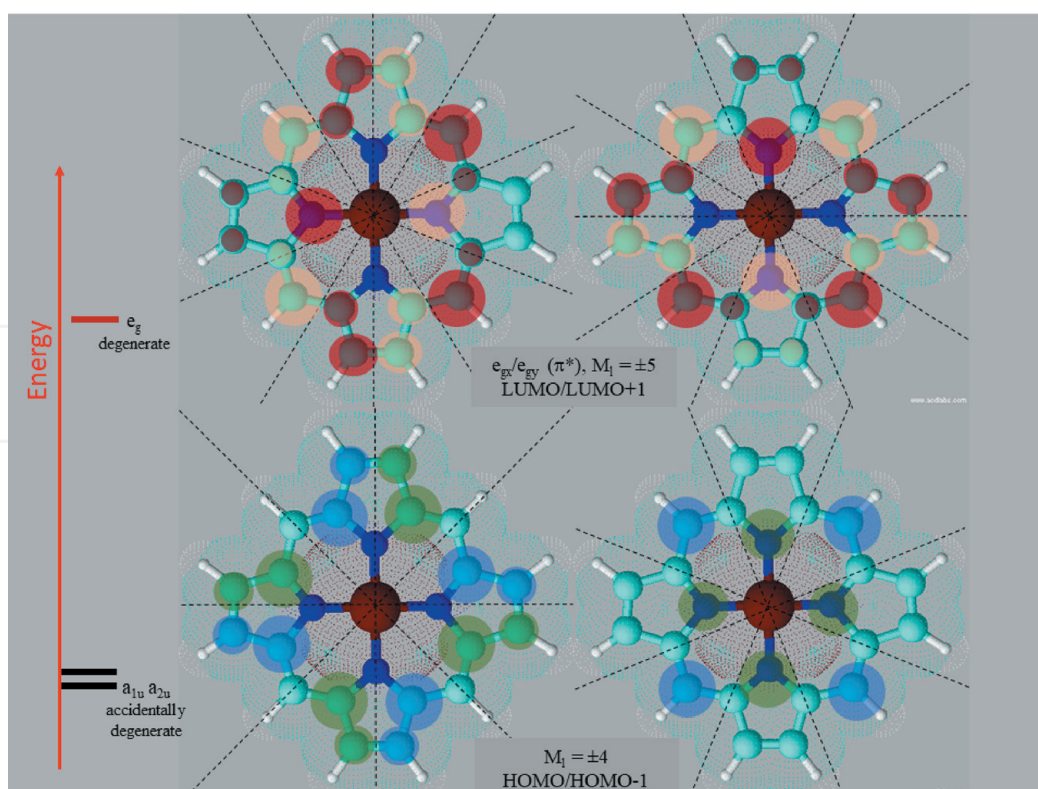
**Figure 1.** Porphyrin structure. (a) Porphine; (b) generic structure of a metalloporphyrin with meso- and  $\beta$ -substituents; (c) iron protoporphyrin IX in oxyhemoglobin and oxymyoglobin exhibiting the heme iron axial ligands, lateral chain of histidine at the fifth coordination position, and molecular oxygen at the sixth coordination position; and (d) structure of chlorophyll, a magnesium porphyrin responsible for light harvesting in the photosynthesis process.

the metal-nitrogen bond of a metalloporphyrin [2, 3]. Carbenes can also be added to the porphyrin ring to form homoporphyrin that is also known as expanded porphyrins [4, 5]. The replacement of a nitrogen by C, O, S, Se, and Te results in core-modified porphyrins that are a platform for organometallic chemistry [6]. Two porphyrins are key groups for the energetic metabolism, oxygen transport, and photosynthesis: the iron protoporphyrin IX, the heme group, and chlorophyll (**Figure 1c** and **d**, respectively).

Metalloporphyrins are found in biological systems as the prosthetic group of proteins. Hemeproteins encompass a diversity of proteins associated with the heme group (iron protoporphyrin IX) such as respiratory cytochromes (cyt), cytoglobins (Cgb), neuroglobins (Ngb), myoglobin (Mb), hemoglobin (Hb), cytochrome P450 (CYP), cytochrome b5 (cytb5), and others [7, 8]. The biological activity of hemeproteins is modulated by the microenvironment and iron axial ligands provided by the apoprotein. The modulation of heme iron properties by the microenvironment of proteins results in the same prosthetic group responding for oxygen transport and storage [9], electron transport,  $\text{NO}^\bullet$  trapping, and a variety of catalytic activities such as redox reactions, hydrogen peroxide cleavage, hydroxylation of aromatic

compounds, and others [8]. **Figure 1c** shows the heme group of hemoglobin with histidine imidazole ring as the heme iron axial ligand at the fifth coordination position and molecular oxygen coordinated at the sixth coordination position. Other important biological metalloporphyrins are chlorophylls (magnesium complexes, **Figure 1d**), the plant pigment responsible for plant light harvesting, and cyanocobalamin, a vitamin B12 (cobalt complex, not shown) that participates in the lipid metabolism [10]. The remarkable chemical and photophysical properties of porphyrins have attracted the interest of researchers worldwide [1]. Biological and technological applications of porphyrins can involve the use of native heme proteins, metallo-substituted heme proteins, and the product of the tryptic digestion of horse heart cytochrome *c*, microperoxidases [11–19]. Inspired by nature, researchers have synthesized a diversity of nonnatural porphyrins. Theoretical studies of porphyrins have also gained relevance [4, 20–23]. Synthesis of porphyrins is principally motivated by improved use in photodynamic therapy, energy, and catalysis [24–26]. The catalytic and photochemical properties of porphyrins are dependent on the presence and type of the central metal ion with axial ligands, the peripheral decoration, and microenvironment of the ring [11, 27]. In this regard, Zhang et al. [27] demonstrated that the peripheral decoration of porphyrins with simple electron withdrawing and donating groups affects the four Gouterman orbitals with a significant impact on spectroscopic properties and functions (**Figure 2**).

For both solar cells and PDT applications, it is essential that the electron promotion to the lowest excited state can be achieved by the absorption of red light. For energy, the chirality is also interesting because of the chiral-induced spin selectivity (CISS) effect. One example is the generation of hydrogen ( $H_2$ ) from water splitting by semiconductors. In a standard water splitting system by a semiconductor, the



**Figure 2.** Schematic representation of the 18  $\pi$  electron aromatic ring of a metallated porphyrin with the four nodes of the HOMOs and five nodes of the LUMOs (black-dotted lines). The ML values of HOMO and LUMO pairs are  $\pm 4$  and  $\pm 5$ , respectively. The electron density of occupied  $\pi$  MOs is represented by the blue and green shading. The red and yellow shading represents the electron density map of the unoccupied  $\pi^*$  MOs (molecular orbitals). Scheme inspired in the study of Zhang et al. [27].



sunlight absorption produces the electron hole pair. The water oxidation by holes ( $h^+$ ) produces hydroxyl free radicals as intermediates of molecular oxygen evolution. The formation of hydrogen molecules requires that protons ( $H^+$ ), resulting from the combination of hydroxyl radicals as molecular oxygen, accept the electrons promoted to the conduction band. However, hydrogen gas production competes with the combination of hydroxyl radicals as hydrogen peroxide that is favored by spin-antiparallel photogenerated holes. In the absence of a spin filter, the combination of spin-antiparallel hydroxyl radicals produces singlet molecular oxygen and requires an overpotential of 1 eV, since molecular oxygen is a triplet species in the fundamental state. Chiral molecules act as a spin filter in the electron transfer favoring the production of spin-parallel hydroxyl free radicals and consequently oxygen evolution simultaneously with  $H_2$  production [28]. In the literature, the association of porphyrins and/or heme proteins with nanostructures, especially for photodynamic therapy purposes, is reported [14, 29]. The reason for this association refers to an enormous quantity of studies and recent findings involving nanostructure properties and manipulation, particularly the potential for drug delivery systems [30]. Nanostructured materials have at least one dimension between 1 and 100 nm. They usually have different (electronic, mechanic, magnetic, optical, etc.) properties from the bulk material, which results in multiple potential applications [31].

## **1.2 General and basic concepts about nanotechnology, nano-/microrobots (motors), and spintronics**

### *1.2.1 Spintronic*

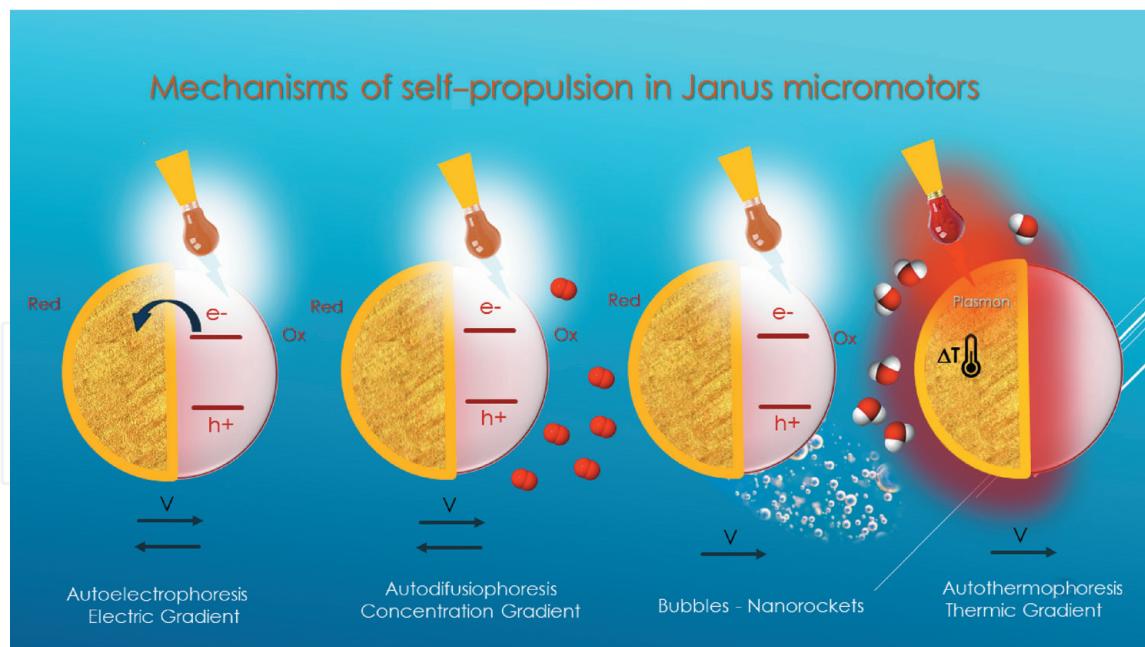
Spintronic concept raised in the late 1980s refers to the use of spins to information transmission and computational operations [32, 33]. Spintronics is an emergent technology grounded in the information transmission by electronic charge and electron spin [34–39]. Spintronic represents a paradigm break in the field of information to combine charge and magnetism in processing and storage. The beginning of spintronics is marked by the discovery of giant magnetoresistance (GMR) effect, in 1988, which resulted in the award of Nobel Prize in Physics in 2007 to Fert and Grunberg [40, 41]. Firstly, spintronic was associated with inorganic oxides, metals, and semiconductors because of the dependence of spin-orbit coupling (SOC). However, organic molecules have wanted properties such as biocompatibility, flexibility, abundance, the possibility of synthesis, low cost [32, 42], and rapidly gained interest in the spintronic studies. The potential applications for spintronics, particularly for electronic devices, are spin filters, spin diodes, spin transistors, spin field-effect transistors, and spin qubits in semiconductor nanostructures [42]. Spintronic has some emerging and promising subfields that are current-induced torque (CIT), spin Hall effect (SHE), spin caloritronics, silicon spintronics, spintronic aspects of graphene and topological insulators (TIs), and chiral-induced spin selectivity effect [32, 34]. The electron spins are degenerate in energy, but the level of degeneracy is broken inside the helix because the electron velocity generates an effective magnetic field that couples with the chiral potential. In a model of DNA double helix, the spin-down electrons aligned preferentially parallel to their velocity in a right-handed helix, while the same occurred with spin-up electrons in the left-handed helix. In an experimental approach, self-assembled monolayers (SAMs) of 3' thiolated single- and double-strand DNAs (ssDNA and dsDNA, respectively) were attached on a clean 200 nm-thick polycrystalline gold film that was evaporated on glass slides. Photoelectrons were ejected from the gold film by clockwise and counterclockwise circularly polarized light and transmitted through ssDNA and dsDNA monolayers. A more intense transport of electrons ejected with

a counterclockwise polarized laser in dsDNA was detected, and no spin selectivity was detected in ssDNA SAMs. Zwang et al. demonstrated that the spin selectivity in DNA is dependent on the supramolecular organization of chiral DNA moieties rather than the chirality of the individual monomers, and thus the spin selectivity can be switched by a conformational change of the molecules [32, 35–39, 43]. The mechanism of CISS effect is believed to be a result of evolution [37], where chiral molecules can increase the conductance of electrons with a spin channel while decreasing the other one [32, 33, 43]. Mishra et al. [44], in recent studies, demonstrated a spin-dependent electron transmission through helical structured bacteriorhodopsin proteins. The study potentially says that the spin degree of freedom may be associated with an important function in electron transport in biological systems. Einati et al. [45] and Roy et al. [46] have shown that the efficiency of electron spin filtering through purple membrane films can be reduced with a green light. So, at potential applications of spin filters, it could modulate the efficiency of the filter.

### 1.2.2 Nanorobots

Nowadays, a new field of study involving nanotechnology is gaining importance: micro-/nanorobotics. Micro-/nanorobots (MNRs) have autonomous motion provided by micro-/nanomotors (MNM) that are micro-/nanometer-scale devices powered with the ability to convert chemical, optical, acoustic, magnetic, and electrical energies into mechanical energy [47]. MNRs can be functionalized to perform complex tasks in a microcosm that constitutes the so-called micro-/nanorobots (MNRs) [48]. MNRs have an extensive range of potential applications such as remediation, nanofabrication, repair of materials, engineering, computing, environment monitoring, and especially in theranostics. Drug delivery systems, cell transport, and DNA and RNA insertions are some of the most numerous studies [49, 50]. The size of MNMs allows their application in minimally invasive diagnosis and treatments [51]. There is a basic classification for nanorobots. They can be biological, artificial, or biohybrid [52]. Also, they are classified according to the type of propulsion: self-propelled or external field-propelled ones. The self-propelled nanorobots convert energy from the environment to kinetic energy for independent movement, and it can be done by self-electrophoresis, self-thermophoresis, self-diffusiophoresis, and tiny bubbles [52]. Among the energy sources that self-propelled MNMs can use, light is highly attractive [47]. Light-powered MNMs can obtain energy from an external source and surrounding chemicals to get efficient propulsion through a photocatalytic process and constitute the photocatalytic micro-/nanomotors (PMNMs). Self-propelling PMNMs can be controlled in various ways such as chemical concentration or light intensity [47, 48, 53]. Furthermore, these PMNMs can be operated at low levels of optical and chemical energy input, which are highly desired scenarios. An important aspect is that the photocatalytic reactions of PMNMs can generate the superoxide radicals ( $O_2^{\cdot-}$ ) that give these devices great potential for environmental remediation, especially in the degradation of organic pollutants. The Janus model can be used to explain the basic principles that respond to the self-propulsion of the photocatalytic MNMs (**Figure 3**).

The external field-propelled MNRs depend on an external force such as electric and magnetic field, light impulses, sonic waves, etc. [52]. The fabrication of MNRs can be direct, indirect, or by self-assembly [51]. The techniques used for the MNR fabrication are the same for the regular nanoparticles: top-down (lithography and scanning probe microscopy) and bottom-up (deposition, a solution with reducing agents). The materials used for MNR fabrication could be super magnetic substances, organic and inorganic compounds, and biological substances [51, 54].



**Figure 3.**

*Self-propelling mechanisms of Janus micromotors. The photocatalytic mechanisms are represented by the three first representations. The formation of a concentration gradient of superoxide ions and bubbles results from the oxidation of hydrogen peroxide in solution. In the right image, irradiation with infrared light on the nanostructured gold layer creates a thermal gradient due to the plasmonic effect. Warming promotes agitation of water molecules that generate one-way movement.*

## 2. Applications of porphyrins and hemeproteins in spintronics

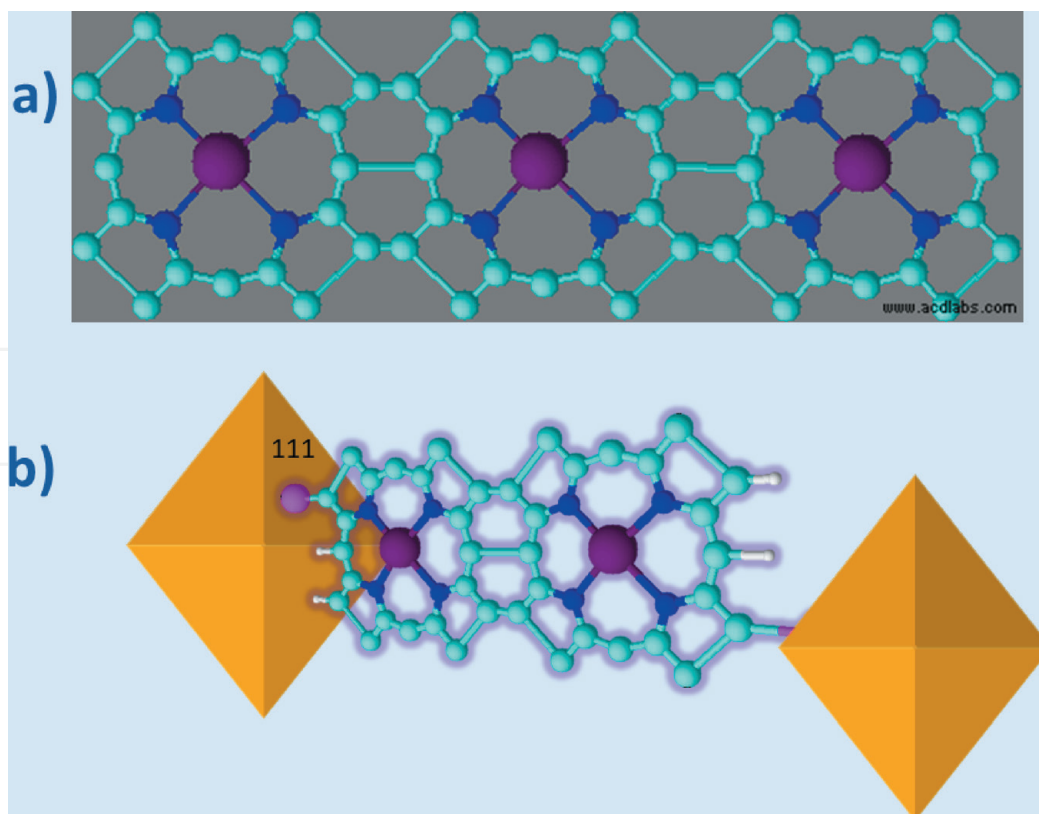
### 2.1 Porphyrins and derivatives

Single-molecule spintronic devices have gained crescent interest for the use in advanced electronic systems. The question is to find molecular structures which, as single molecule, can exhibit the desirable properties of spintronics such as spin valve [55–60], spin crossover [61–63], spin filtering [64–66], Kondo effect [67], and others. In the literature, porphyrins and derivatives have been described as promising candidates for molecular devices, once they have unique electronic properties [68]. Theoretical and experimental studies on the charge transport of porphyrin-based derivatives have demonstrated desirable physical properties for single-molecule spintronic such as current switching, long-range electron tunneling, current rectifying, and others [55, 69–71]. Several studies have corroborated the potential of porphyrin application in spintronics. Self-assembled porphyrin nanorods showed the mediated conduction through a UHV-STM image with differing HOMO- and LUMO-mediated conductions. The authors demonstrated a conductivity by barrier-type tunneling through distances less than 10 nm and long-distance conduction occurring only through the LUMO band. The self-assembled porphyrin nanorods are an efficient rectifying device that converts alternating current (AC), i.e., a current that periodically inverts direction, to direct current (DC), which moves in a unique direction [72]. In another study, the electronic transport of a nanowire composed by porphyrin-ethyne-benzene conjugates had its effective conductivity assigned to the coplanar conformation of phenyl and porphyrin moieties. The coplanar structure that allows amino or nitro substituent at the meta-position of the phenyl bridge that connects the  $\pi$ -system can provide higher current ratios of the on/off states. The switch effect of meta-substituents in the coplanar conformation disturbs the whole molecule



while having only a local impact on the system with a perpendicular conformation. The nanowires formed by  $\pi$ -conjugated systems have potential for switch devices tunable by substituents [69]. Another evidence of porphyrin application in electronic devices was reported by Sedghi et al. [71]. Nanowires formed by porphyrin molecules linearly oligomerized (oligo-porphyrin wires) can mediate temperature-dependent electron transport. The study showed that the system conductance has temperature dependence and it suggests a long-range electron tunneling [71]. For application in spintronic devices, Cho et al. [73] proposed a theoretical organometallic framework formed by one-dimensional infinite chromium porphyrin array in which chromium atoms are located in a straight line (**Figure 4a**). The system exhibited spin filter property when the simulations were carried out with dimeric form, Cr-PA<sub>2</sub>, between Au electrodes (**Figure 4b**).

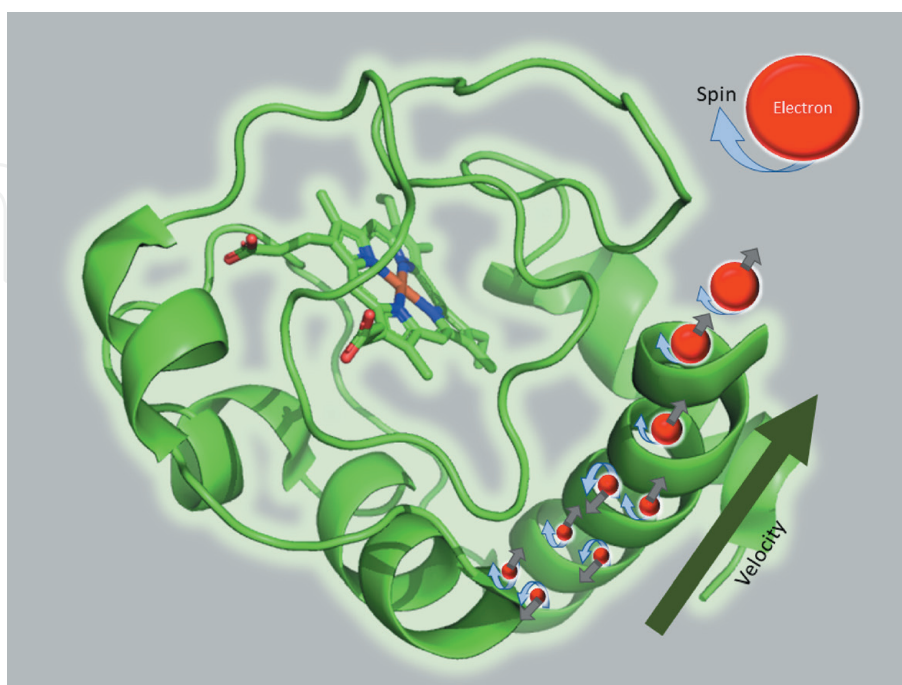
The fabrication of spin-dependent electronics, the spintronic devices, requires the external control of the magnetization of the that behaves like a magnet. In this regard, the paramagnetic porphyrin molecule is a promising active building block for spintronic devices. Wende et al. [74] studied by experimental and theoretical approach paramagnetic iron porphyrin molecules bound on ferromagnetic Ni and Co films on Cu(100). The authors investigated the porphyrin structural orientation and the magnetic coupling with the substrate. The porphyrin molecules associated with the substrate Co or Ni were ordered ferromagnetically. In the device, the magnetic moment of the porphyrin iron could be rotated in the plane and out of the plane by a magnetization reversal of the substrate. In a similar study, Scheybal et al. [75] also associated porphyrins with metallic films and studied X-ray magnetic circular dichroism (XMCD). In this case, the researchers used manganese (III)-tetraphenylporphyrin chloride (MnTPPCL) molecules adsorbed by cobalt substrate



**Figure 4.** Examples of nanowires formed by porphyrins. (a) Theoretical organometallic framework built by one-dimensional infinite chromium porphyrin array in which chromium atoms are parallel, the M-Pan; (b) a dimeric form, Cr-PA<sub>2</sub>, linked to two Au (111) electrodes PA<sub>2</sub> via Au-S bond. Structures of nanodevices modified from Cho et al. [73].



film. The results demonstrated that the film substrate induced a net magnetization on the porphyrin. Chen et al. [76] made calculations of conductance in a ferrous porphyrin. The study showed that the conductance of the iron porphyrin is tuned by mechanical distortion of the porphyrin plane and shifts the coupling state from the low spin to excited spin states. These properties of the system are interesting for sensing applications. Systems containing molecules with switchable spins are promising for the fabrication of materials with spintronic properties. Organometallic molecules such as porphyrins can be switched to on and off magnetic states when associated with the ferromagnetic substrate. Wäckerlin et al. [77] described that cobalt(II)tetraphenylporphyrin (CoTPP) ferromagnetically coupled to nickel thin film (Ni(001)) is switchable from on to off state of Co spin by the complexation with NO that is a spin trans effect. NO coordinates with  $\text{Co}^{2+}$  leading to the formation of a NO-CoTPP nitrosyl complex that is the off state of the Co spin. The system is restored to the *on* state when NO is thermally dissociated from the nitrosyl complex. Li et al. reported the construction and magnetic characterization of a fully functional system formed by the hybridization of a single magnetic porphyrin molecule with graphene nanoribbons. The fusion of the porphyrin core into graphene through the formation of new carbon rings at chemically predefined positions was demonstrated by scanning tunneling microscopy of high resolution. The authors also demonstrated that porphyrin retains the magnetic functionality and the magnetic anisotropy is modulated by the structure of the contacts [78]. In another study, Lewandowska et al. report a simple and efficient method for the fabrication of porphyrin-graphene oxide hybrids. The hybrid system has donor-acceptor properties and exhibits charge transfer between porphyrin and graphene oxide. The non-covalent interaction between the porphyrin and graphene oxide changes intensely the magnetic properties. The dramatic change in the magnetic properties probably is due to refined tuning of graphene domain magnetism that can be promoted by the modulation electron density produced by electron donor or electron acceptor substituents [79].



**Figure 5.** Chiral-induced spin selectivity (CISS) effect in cytochrome *c*. cartoon of the spin-filtered electron transport through the chiral  $\alpha$ -helix of cytochrome *c* as reported by Michaeli et al. [82]. Horse heart cytochrome *c* structure was obtained from protein data Bank, code 1HRC.

## 2.2 Hemeproteins

The presence of the iron protoporphyrin IX as the prosthetic group of heme-proteins endows these proteins of electronic and magnetic properties that can be applied in spintronics. The hemeproteins have an additional property that is the folding in chiral structures. [80]. The chiral structures such as the  $\alpha$ -helices present in cytochrome *c* (**Figure 5**), for instance, can act as spin filters and respond for the chiral-induced spin selectivity (CISS) effect. To date, cytochrome *c* has been the unique hemeprotein used for spin filtering [28, 33, 38].

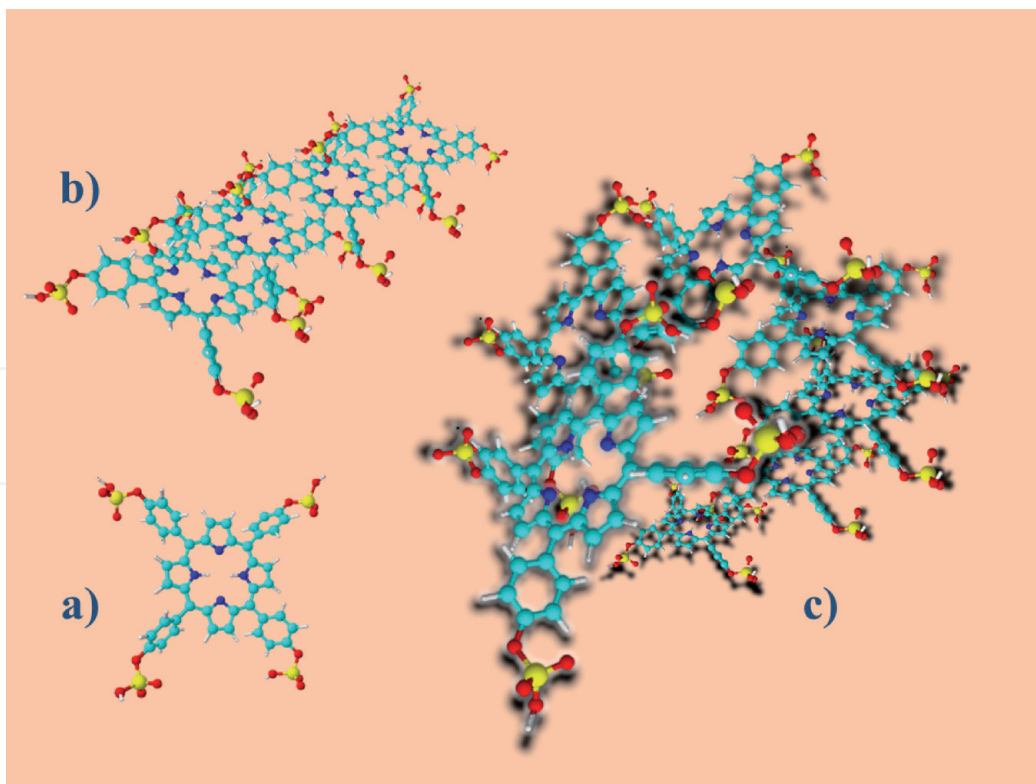
New types of spin-dependent electrochemistry measurements have been applied to probe the spin-dependent charge transport properties of nonmagnetic chiral molecules such as cytochrome *c*. Besides cytochrome *c*, the photosystems that are complexes of proteins associated with a non-heme porphyrin, the chlorophyll, also have electron transport capacity with spin selectivity [81, 82]. When the measurements were carried out with different orientations of the PSI protein complex, the dependence of spin polarization with the electron transfer path in photosystem I was proven [81, 82].

## 3. Application of porphyrins and hemeproteins in the construction and working of micro-/nanorobots

### 3.1 Porphyrins and derivatives

Several studies have been developed to produce nanodevices containing porphyrins with a potential use in MNRs to be applied in theranostics. According to Li et al. [83], porphyrins have a diversity of properties applicable to health preservation, diagnosis, and treatment. Porphyrins can amplify signals for magnetic resonance imaging (MRI), positron emission tomography (PET), infrared fluorescence imaging, and dual modal PET-MRI. Porphyrins have chemical and physical properties that allow the application of these compounds in the detection and destruction of tumors. Porphyrins can efficiently convert light into electronic excitation of molecular oxygen to produce singlet oxygen in photodynamic therapy (PDT) or light to heat for photothermal therapy (PTT). Therefore, porphyrins have been applied in the treatment of solid cancers and ocular vascularization diseases [29]. Also, there are some studies about porphyrin-nanoparticle systems employed in dentistry treatment [84–87]. These systems can be used in the diagnosis of cancer by acting, for instance, as biosensors that exhibit affinity for a single molecule converting biochemical to electrical signals, detection of salivary biomarkers of oral tumors, and others [85, 88]. The capacity of self-assembly in a range of supramolecular aggregates is a crucial property for the application of porphyrins to construct MNRs [29, 89]. Ion et al. [89] demonstrated that porphyrins could self-assemble in several types of supramolecular aggregates such as linear head to tail, J-aggregates, and fractal aggregates with diverse and definite photophysical properties (**Figure 6**) [89].

The study of Ion et al. showed nanotubes formed by porphyrins and the importance of this technique for brain aneurysm instrumentation. They used meso-5, 10, 15, 20-sulfonate-phenyl porphyrin (TPPS4) and observed the formation of organized nanostructures by ionic self-assembly. Neurons and glial cells incubated with porphyrin nanotubes formed interconnected networks featured on the nanotube templates. The capacity of TPPS4 to form nanotubes by self-assembly demonstrates the potential of this porphyrin in the fabrication of MNRs applied to medicine. MNRs must have the capacity to self-propel that could be provided by a diversity of materials and mechanisms. Park et al. describe the fabrication of “swimmers”: microstructures with autonomous mobility at water/air interface. The particles of porphyrin-based



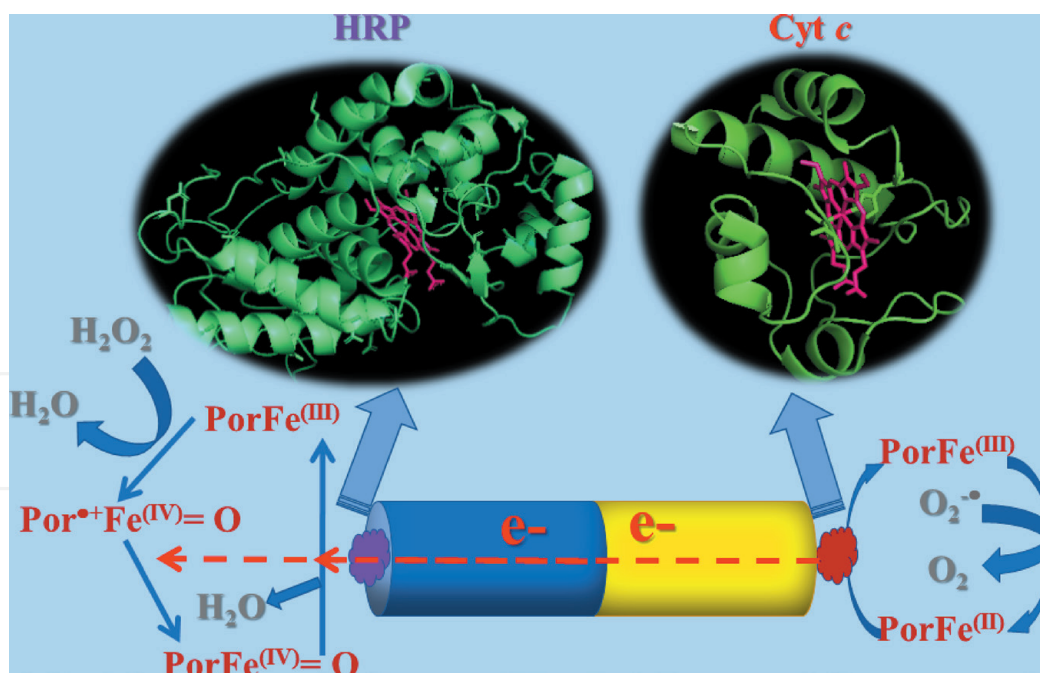
**Figure 6.** Supramolecular aggregates of meso-5,10,15,20-sulfonate-phenyl porphyrin (TPPS<sub>4</sub>). (a) The free-base monomer of TPPS<sub>4</sub>, (b) the head-to-tail linear self-assembly of TPPS<sub>4</sub>, and (c) the J-aggregate of TPPS<sub>4</sub>.

metal–organic frameworks (MOFs) were fabricated with hydrophobic meso-tetra (4-carboxyphenyl)-porphyrin (H4-TCPP-H2, L) ligands bound to Zr-oxo clusters. The H4-TCPP-H2, L responds for the hydrophobic character of the framework [90]. Similar MOFs were described in the literature before, once they are efficient in the controlled release of surface-active substances proportionating a controlled motion. However, usually, the MOFs use high-cost surface-active substances [90]. The MOFs fabricated with meso-tetra(4-carboxyphenyl)-porphyrin ligands bound to Zr-oxo clusters use much less expensive fuels. The particles have the advantage to be refueled multiple times and attained speeds of ca.  $200 \text{ mm}\cdot\text{s}^{-1}$ . Interestingly, the type of fuel, the microstructure, and surface wettability of the MOF surface determine the efficiency of motion. In another study, Serrà et al. [91] reported the fabrication of a multifunctional nanorobotic platform with magnetic properties to promote the death of cancer cells by magnetic and mechanical destruction. A multi-segmented nanowire composed by nickel and gold alternating segments was produced by electrodeposition of metals inside the nanochannels of a polycarbonate membrane. In sequence, the nickel segments were transformed in core-shell Ni/NiO segments by the treatment of the nanowire with NaOH 0.5 M for 6 h. The nanowires were treated sequentially with zinc protoporphyrin IX and 1,9-nonanedithiol that displaces the porphyrin from the gold segments. The nanotubes exhibited ferromagnetism and could be manipulated by a magnet. When the bi-functionalized nanotubes attain cells, magnet or photo-stimulation can induce cell death that is useful for cancer treatments since the effect of some medical procedures, like hyperthermia and photodynamic therapy, could be improved by application of a rotary magnetic field [91].

### 3.2 Hemeproteins

Hemeproteins such as hemoglobin (Hb), myoglobin (Mb), horseradish peroxidase (HRP), catalase, and cytochrome *c* (cyt *c*) have the prosthetic group, ferrous or





**Figure 7.** Proposed bio-electrochemical mechanism behind the enhanced diffusive motion of (HRP)PPy-Au(cyt *c*) nanorods in  $O_2^{\cdot-}$  and  $H_2O_2$  solutions. Native HRP ( $PorFe^{(III)}$ ) reduces  $H_2O_2$  to water and is converted to compound I ( $Por^+Fe^{(IV)}=O$ ), while ferric cyt *c* ( $PorFe^{(III)}$ ) is reduced by  $O_2^{\cdot-}$ . Ferrous cyt *c* ( $PorFe^{(II)}$ ) recycles to the ferric form by transferring electrons through the PPy-Au nanorod to HRP compound I ( $Por^+Fe^{(IV)}=O$ ) and compound II ( $PorFe^{(IV)}=O$ ) that recycles to native HRP. The structures of HRP and cytochrome *c* were obtained from protein data Bank (1HCH and 1HRC, respectively). Mechanism from Pavel et al. [97].

ferric protoporphyrin IX (heme group), as the redox center. The heme group makes hemeproteins useful for a medical and technological application that involves redox reactions. The use of hemeproteins in nanodevices can be impaired by denaturation or the orientation of the redox site [92]. However, literature has several examples of the use of hemeproteins in nanodevices [93–95]. Hemeproteins can also be used in the self-propelling of MNRs. Hemeproteins can act in MNMs by the bubble recoil mechanism. Catalase is the best hemeprotein for use in MNMs due to the capacity to convert hydrogen peroxide to oxygen generating propulsion bubbles [96]. Pavel et al. [97] fabricated nanorods with self-electrophoresis taking advantage of the combined catalysis of HRP and cytochrome *c* as illustrated in **Figure 7**.

One half of the nanorod was made of polypyrrole (PPy) modified with HRP, and the other half was made of gold and decorated with cyt *c*. [97]. The charge separation was promoted by the reaction of cytochrome *c* with superoxide ion ( $O_2^{\cdot-}$ ) and HRP with  $H_2O_2$ . Ferric cyt *c* oxidizes  $O_2^{\cdot-}$  to  $O_2$  and is recycled to the oxidized form by transferring one electron through the nanorod to the high valence forms of HRP generated by the reaction with hydrogen peroxide (**Figure 7**) [97]. The study published by Pavel et al. demonstrated that the hemeproteins are robust enough to maintain the activity even immobilized on solid substrates [97].

#### 4. Conclusions and perspectives

Porphyrins and hemeproteins have been widely studied because of their biological roles in energy metabolism and light harvesting in photosynthesis. More recently, with the advancement of bioelectronics and micro-/nanorobotics, porphyrins and hemoproteins have gained interest because of their specific properties. Porphyrins have desirable properties for single-molecule spintronic such as current switching, long-range electron tunneling, current rectifying, and others.



Regarding the hemoproteins, they combine the presence of a porphyrin (iron protoporphyrin IX) as the redox center with the chiral protein structure that acts as a spin filter. To date, cytochrome *c* stands out as the hemoprotein for which the capacity to produce CISS effect has already been demonstrated experimentally. Porphyrins and hemoproteins also have proven potential for nanorobotic application. Porphyrins are particularly useful for nanorobotics applied to medicine because of their photochemical properties. Porphyrins also can self-assemble in structures such as J-aggregates to form nanotubes. On the other hand, the catalytic properties of hemoproteins are the most relevant factor that makes them applicable to self-propulsion in micro-/nanorobotics. The studies and applications of porphyrins and hemoproteins in spintronic and nanorobotic are still in their early stages, and a wide field of study of these compounds is open to the area of bioelectronics. Among the numerous advances that are possible for the field of spintronic, special attention has been given to spinterface, that is, the interface between a ferromagnetic (FM) metal and an organic semiconductor, in which unique hybrid states are formed. The FM metal/molecular interfaces constitute an important building block for the future of spintronics. The unique hybrid states of spinterfaces influence magnetic properties such as magnetic anisotropy, magnetic exchange coupling, interfacial spin polarization, and others. Further, the interactions between the FM metal and organic molecules are tunable in such a way that the spinterfaces are applicable to multifunctional devices meeting the industry tendency of miniaturization using single-molecule devices. The external control of spinterface by external signals, especially light because the ultra-fast optical transmission, is a promising area for future investigations. An important challenge for the design of spintronic devices is the changeable control and switch of single molecules adsorbed on the surface of FM materials. Particularly, for the metalloporphyrins, an interesting example is the use of axial ligands of the porphyrin transition metal center to change the magnetism of the molecular component [98]. NO<sup>•</sup> was able to reversibly switch the spin state of the Co and Fe of porphyrins adsorbed on Ni(001) Co substrates, respectively. Similarly, NH<sub>3</sub> was able to induce the transition of Ni porphyrin on Co substrate from low to high spin states [99, 100]. Another emerging field of spintronics is the use of antiferromagnets that are affected by spin-polarized currents. Antiferromagnetic materials have several advantages for spintronics such as they do not create external magnetic fields and only weak interactions occur with each other and the antiferromagnets have the characteristic frequencies of switching between their states significantly higher than the values obtained for ferromagnets. Further, the occurrence of ordering in antiferromagnets it is more frequent and occurs at soft conditions than in ferromagnets. Also, these materials can behave as a conductor for a spin polarization and as an insulator for other spin polarization. The antiferromagnets can provide desirable characteristics for spintronics that are high speed of operation in terahertz range, performance, easy manipulation, high sensitivity, and low energy cost [101].

The field of micro/nanorobotics that also can take advantage of the properties of porphyrins and hemeproteins has as the principal challenge for advances as the control and powering of the movement. The crescent interest in the application of MNR in theranostic poses the additional challenge for the use of biocompatible and high-performance materials and fuels. An interesting alternative regarding the elimination of toxic fuels is the use of systems having the propulsion powered by external field that are fuel-free and allow the remote control of the movement. The MNRs with a real potential to operate *in vivo* are rare now and constitute an important area for future investigations that requires multi- and interdisciplinary studies [102].

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## **Conflict of interest**

The authors declare no conflict of interest.

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