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# Hybrid Porphyrin-Polymeric Materials and their Amazing Applications: A Review

Gheorghe Fagadar-Cosma[1], Mihaela Birdeanu[2,3] and Eugenia Fagadar-Cosma[3,*]

[1]"Politehnica" University of Timisoara, Vasile Parvan Street 6, 300223-Timisoara, Romania

[2]National Institute for Research and Development in Electrochemistry and Condensed Matter, 1 Plautius Andronescu Street, 300224 Timisoara, Romania

[3]Institute of Chemistry Timisoara of Romanian Academy, M. Viteazul Ave. 24, 300223, Timisoara, Romania

**Abstract:** Porphyrins are versatile multifunctional biomimetic molecules that are obtained by condensation of pyrrole with the desired aromatic aldehydes. The porphyrin structure can be synthetically modified by either introduction of various peripheral functional groups or metals in its core, allowing creation of various porphyrin derivatives that exhibit amazing optoelectronic properties. This feature makes porphyrins molecules extremely useful especially in hybrid combination with photonic, electronic and magnetic compounds. This review is focused on the more recently obtained porphyrin-polymeric materials and on their various analytical, industrial and medical applications. The study underlines the assembling capacity of these porphyrin-polymer hybrids to form supramolecular tunable architectures by means of the association of more building block units. Porphyrin-polymer nano- and micro-materials play a preeminent role in sensing applications involving chromophores in the formulation of organic solar cells - due to their capacity to generate photo induced charge separation centers - and as new materials with interesting catalytic properties. Besides these technical applications, the photobactericidal activity of these porphyrin–polymer materials was evaluated against Gram positive and Gram negative strains bacteria and they represent an alternative to antibiotics in order to overcome the growing bacterial multiresistance. Polymer functionalization with porphyrin is commonly used to overcome some drawbacks such as self-quenching and photo-toxicity to the skin produced by the bare porphyrins, when used as photosensitizers in the non-invasive Photodynamic therapy of cancer (PDT).

**Keywords:** Porphyrin-polymer hybrids, aggregates, sensors, catalysts, medical applications.

***Dedicated to Anniversary of 150 years since the establishment of Romanian Academy***

## 1. INTRODUCTION

Porphyrins and their derivatives are versatile multifunctional biomimetic molecules and their importance for life, medicine and industry as has been recognized by offering the awards of the Nobel Prizes in Chemistry in 1915 (to Richard Willstätter for his researches on plant pigments, especially chlorophyll), 1930 (to Hans Fischer for his researches into the constitution of haemin and chlorophyll and especially for his synthesis of haemin), 1961 (to Melvin Calvin for investigations on the carbon dioxide assimilation in plants), 1962 (*ex aequo*to Max Ferdinand Perutz and John Cowdery Kendrew for elucidations of the structures of globular proteins), 1965 (Robert B. Woodward for his outstanding achievements in the art of organic synthesis and especially for first total synthesis of Chlorophyll) and 1988 (jointly to Johann Deisenhofer, Robert Huber and Hartmut Michel for the determination of the three-dimensional structure of a photosynthetic reaction centre) [1].

Porphyrins and their derivatives are large hydrophobic π-conjugated tetrapyrrolic compounds and as a consequence promising organic building blocks that provide amazing tunable optoelectronic properties. Based on earlier remarkable above mentioned achievements, porphyrins became indispensable for obtaining of nanostructured materials with wide applications in electrochemical coatings [2], sensors [3], selective catalysts [4] and bio-catalysts [5, 6], color imaging [7], drug delivery [8], treatment of cancer in medicine [9], neuroprotection [10], pharmaceutical detection of cells, toxins and viruses [11], photodetectors [12], optoelectronics [13] and organic solar cells (named also Gratzel cells [14]. The techniques used in nanotechnology to immobilized porphyrins are: adsorption, entrapment, encapsulation, cross-linking, and covalent bonding. Porphyrins possess huge capacity for chemical modifications by changing the position and varying the substituting functional groups in order to improve their hydrophilic properties and enhance their responses.

On the other hand, polymers have received great attention in coordination chemistry because of their potential applications and intriguing architectures and topologies especially due to their chemically adjustable porosities and high internal surface areas.

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*Address correspondence to this author at the Institute of Chemistry Timisoara of Romanian Academy, M. Viteazul Ave. 24, 300223-Timisoara, Romania; Tel: +40 256491818; Fax: +40 256491824; E-mail: efagadar@yahoo.com

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Porphyrin-polymer complexes were extensively used in the last decade for both various analytical, industrial and medical applications and also for developments in theoretical chemistry [15].

Many reports underlined the assembling capacity of these polymer-porphyrin hybrids to form supramolecular tunable architectures by means of the association of more building block units through covalent bonds, electrostatic forces or weak Van der Waals interactions [16]. These hybrid nano- and micro-materials found various applications in detection and capture of gases [17].

Polymer-porphyrin systems are used as organic dyes in the formulation of solar cells [18] and generate photoinduced charge separation centers. The chemical structure and aggregation capacity of the dye have the main influence on the photocurrent enhancement. Polymer solar cells received attention because of the recent development of flexible electronic devices. The composite films based on conductive polymer polythiophene and 5,10,15,20-tetra (3-thienyl) porphyrin generated resultant photocurrent densities limited by both the chain-length of obtained electropolymerized polythiophenes and the electron mobility in composite films. If the film had a homogeneous structure it showed remarkable enhancement of photocurrent [19].

During the last four decades analytical chemistry used porphyrins and metalloporphyrins that are incorporated into several polymeric films or membranes, such as: PVC [20], polysiloxanes [21], Nafion [22], polymethacrylates [23], polypyrrole [24] or chemically bonded to the polymer chain, such as PVP [25] for the detection or monitoring the presence of different analytes from gases to toxic heavy metals.

Another way to obtain functional porphyrin–polymers is the immobilization of metalloporphyrins substituted in meso positions with fluorene or9,90-spirobifluorene groups by electropolymerization in order to tailor materials with interesting catalytic properties. The three dimensional insoluble materials can be reused several times without losing the catalytic properties of bare metalloporphyrin [26].

## 2. SUPRAMOLECULAR CHEMISTRY OF PORPHYRIN SYSTEMS

Porphyrins are capable to aggregate in various geometries, such as: pyramids, rings, lamellar triangles, straw-like structures, columns and roof-like architectures [27].

Reported data stated [28] that the J aggregates (edge-to-edge stacked) layered on different substrates, such as glass, quartz or silica, aregiving porphyrin uniform films. H-bonding interactions are usually responsible for generating crystalline systems. The main factors that influence the aggregation of porphyrins are the specific structure of the macrocycle, the concentration [29] and the nature of the solvent [30].

Meso-pyridyl substituted porphyrins and Zn metalloporphyrins were used as building blocks for obtaining of multi-porphyrin arrays [31] because of the central metal–N axial coordination bonding interaction. Supramolecular systems based on porphyrin

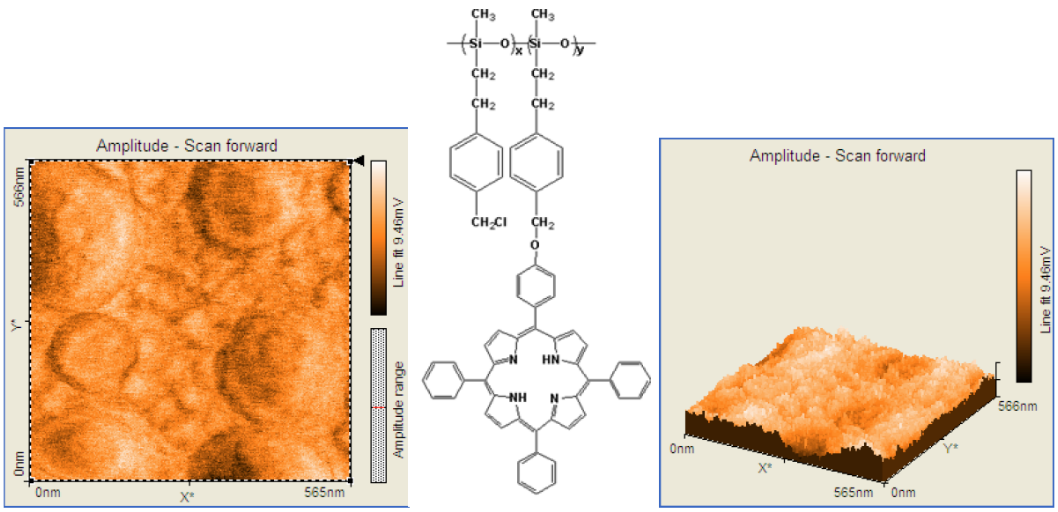

**Figure 1:** 2D and bi-dimensional 3D representation of non-contact mode AFM of porphyrin-grafted on polysiloxanede posited as film on pure silica plates.

derivatives require host-guest interactions and proved to be useful in drug release [32], detection [33] and photocatalytic systems [18].

A porphyrin- grafted on side-chain of a polysiloxane [21] offers vesicular type morphology with particles ranging in diameter between 35 nm and 143.5 nm (Figure **1**).

The spongeous structure of the functionalized polysiloxane material, with uniformly dispersed andlarge globular pores, might be obtained as a result of a reorganization process, accompanied by compression after releasing of the solvent (Figure **2**).

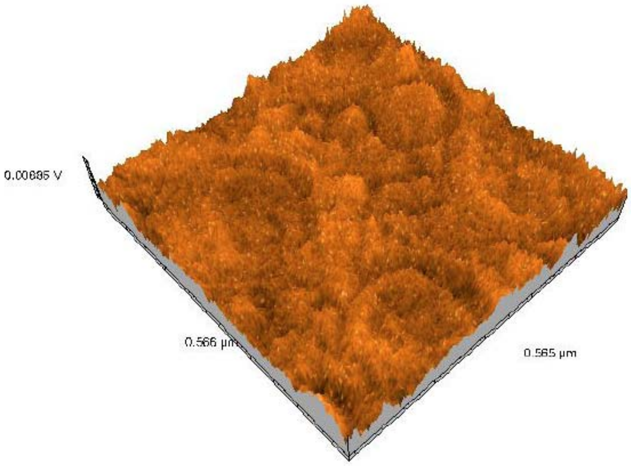

**Figure 2:** 3D AFM image of the porphyrin-grafted on polysiloxane (soft NanoSurf EasyScan2).

## 3. POLYMER-PORPHYRIN SYSTEMS IN SENSING APPLICATIONS

In the last decade, nanoscience and nanotechnology developments are based on demands regarding the capacity of organic compounds to generate various supramolecular structures by assembling the molecules into complex 2D or 3D architectures. From this point of view, porphyrins, that have both optimal structures for π-π interactions and for side-by-side aggregation due to various peripheral substitution, offer the most versatile nanostructures: columns, sheets, tubes, wires along with miscellaneous geometry aggregates [34]. These assemblies offer both selectivity and sensitivity performances for the sensors that are based on porphyrins, which cannot be achieved from single molecules.

### 3.1. Gas Sensors

The surface morphology of the polymer –porphyrin material can affect the sensing mechanism. It is well know that the interaction of the gas molecules starts with the interaction of the active adsorption sites on the surface and then continues with deeper diffusion into the material structure. Thus, studying the surface morphology can help understanding the interaction mechanism between the hybrid material and the gas molecules.

Porphyrins are potential materials for volatileorganic compounds (VOCs) detection, because of their high sensitivity and reversibility.5,10,15,20-tetrakis[3,4-bis(2-ethylhexyloxy)phenyl]-21H,23H-porphine was chosen as sensing material in multilayer Langmuir-Schaefer thin films with poly(methyl methacrylate) and several 4-tert-Butylcalix[n]arenes. UV-visspectroscopy was performed to determine the changes associated with the porphyrin upon exposure to more carboxylic acids [35]. The acetic acid vapor produced the greater response than the butyric acid and the hexanoic acid. The lowest response was given by hexanoic acid due to its long alkyl chain that reduces the binding strength between the acid group and the porphyrin.

Another type of porphyrin, an $A_3B$ mixed functionalized porphyrin: 5-(4-pyridyl)-10,15,20-tris(4-phenoxyphenyl)-porphyrin was incorporated into polyvinylpyrrolidone, a biocompatible polymer, with the purpose to prepare water soluble polymer-dye hybrids**.** The interaction between $CO_2$ and this type of polymer-dye hybrids was studied by UV-vis spectroscopy and the continuous hypochromic response of the Soret band in direct relationship with increased $CO_2$ concentration was noticed. The authors [25] stated that based on the UV-vis spectral differences between the hybrids in acidic medium and during $CO_2$ exposure the mechanism of $CO_2$ detection was not based on pH changes. TEM and AFM analysis gave chances to presuming a mechanism based on chemisorption phenomena which modify the surface properties.

2D and 3D AFM *surface imaging* of hybrids casted on silica plates before $CO_2$ exposure show porous nanomaterials. This is also certified by the topography images, putting into evidence the existence of pores of various dimensions with low degree of organization and of different depths. The aspect of the initial 5-(4-pyridyl)-10,15,20-tris(4-phenoxyphenyl)-porphyrin-polyvinylpyrrolidone hybrid material is sponge like with numerous large volumes of pores (Figure **3**).

Particle analysis reveals that the particle dimension is ranging from 40 to 53 nm, similar with the hydrodynamic size of the aggregates in water solution.

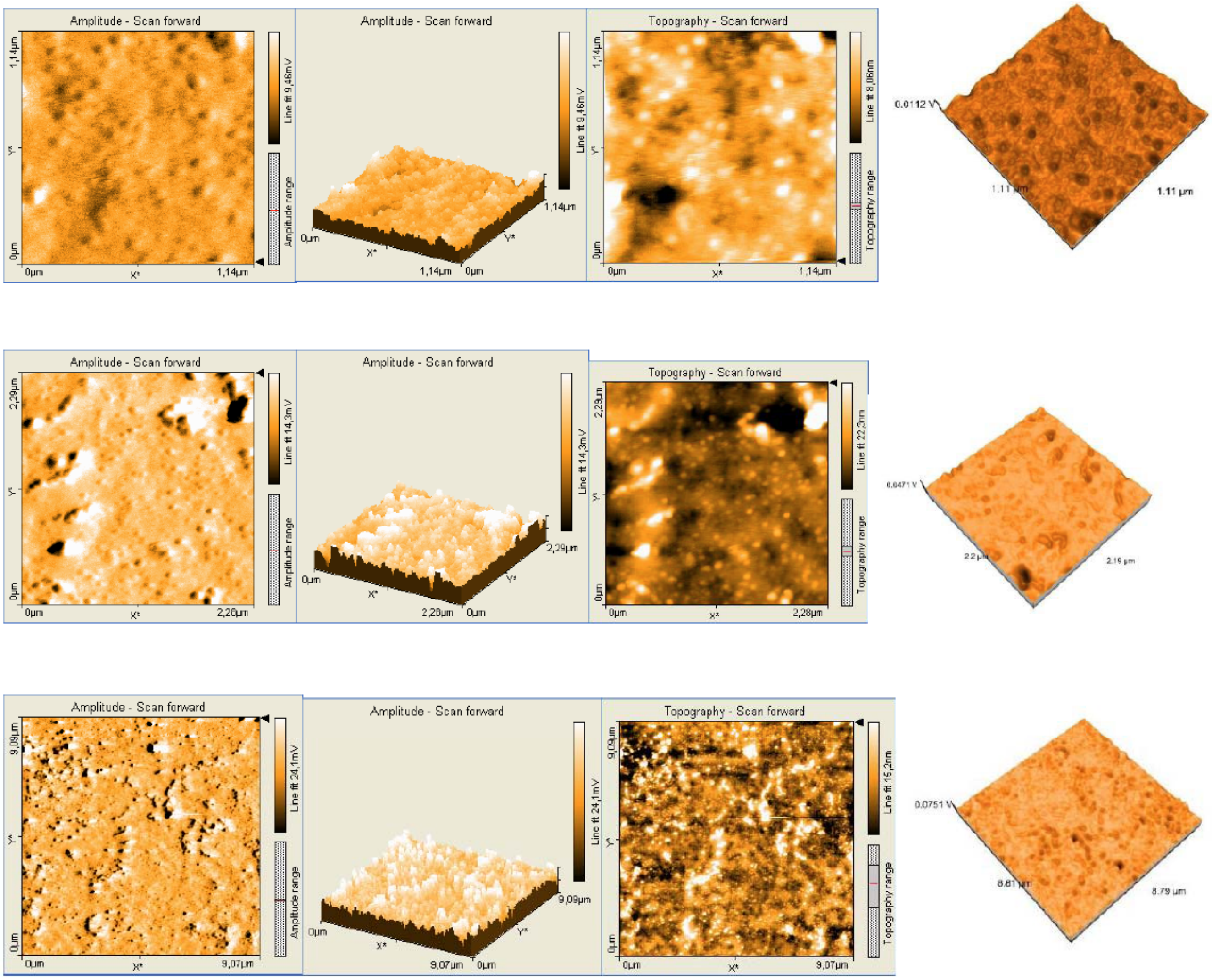

**Figure 3:** Non-contact mode AFM images (1 µm × 1 µm), (2 µm × 2 µm) and (9 µm × 9 µm), 2D representation of 3D map, topography and 3D representation of PVP-PyTPOPP *hybrid 2* before $CO_2$ exposure.

The surface roughness of polymer was varying from 1.2 nm to 1.9 nm and 2.2 nm in films casted on dimensions (1 µm × 1 µm), (2 µm × 2 µm) and (9 µm × 9 µm) respectively. This increase in the surface roughness was favorable for the sensing applications as it increases the overall surface area of the sensor film.

The maximum peak height is in the range of 12 nm to 39 nm and the valley depth is varying from -7.3 nm to -15 nm. The height distribution is varying from 19 up to 90 nm.

After the exposure to $CO_2$, significant changes regarding the morphology and the topography of the PVP-porphyrin hybrid surface can be noticed (Figure **4**). The roughness is ten times decreased after $CO_2$ exposure and varies between 0.19 and 0.26 nm and the maximum peak height is in the range of 1.4 and 4.1 nm, almost 9 times smaller than in initial hybrid. The height distribution is from 7 up to 52 nm also significantly decreased in comparison with unexposed to $CO_2$ material. After $CO_2$ exposure the material has a significant decrease of the number of pores, and their volume is also strongly diminished but a number of straw-like aggregates not evenly distributed are formed probably due to chemisorption process of $CO_2$ (filling of the pores) accompanied by the rearrangement of surface structure.

These water soluble porphyrin-PVP hybrid nanomaterials offer the possibility for developing optical and colorimetric sensors for monitoring $CO_2$ in environment, food and clinical trials.

A completely distinctive class of inorganic–organic hybrid nanomaterials obtained by self-assembling is the class of coordination polymers. Due to the possibility of tailoring their porosities and surface areas these kind of porphyrin-hybrids have valuable

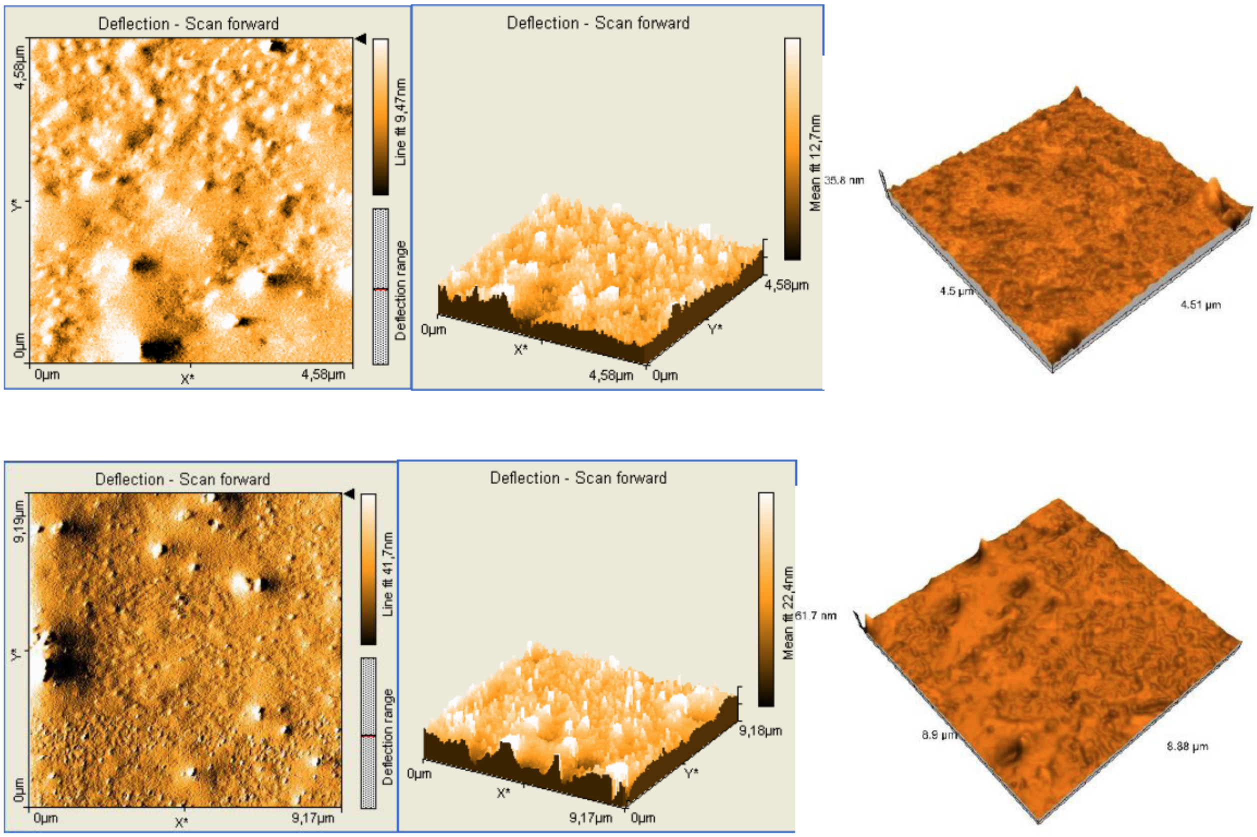

**Figure 4:** Contact mode AFM images (4 µm × 4 µm) and (9 µm × 9 µm), 2D representation of 3D map, and 3D representation of PVP-PyTPOPP *hybrid 2* after $CO_2$ exposure.

applications in catalysis, chromatography and gas storage [31].

### 3.2. Toxic Metal Sensors

$Hg^{2+}$ ions are known that can harm the human nervous system by subsequently accumulation through the food chain. A novel copolymer was obtained by radical copolymerization of 5-(p-acryloyloxyphenyl)-10,15,20-triphenylporphyrin and N,Ndimethylacryl-amide [36] and was reported to selectively detect traces of $Hg^{2+}$ ions with a low detection limit of 50 nM. The optical properties of the polymer, monitored by UV-vis spectroscopy in aqueous solutions revealed a new peak at 456 nm in the porphyrin Soret band and produced also a visible color change from brown-red to green. The possible mechanism was assumed to be based on the formation of aggregates between mercury ion and the porphyrin core.

Two functionalized porphyrins: 5, 10, 15, 20-tetrakis (3,4-dimethoxyphenyl) porphyrin and 5, 10, 15, 20-tetrakis(3-hydroxyphenyl)porphyrin were used as ionophores for preparing PVC-based membrane sensors selective to $Ag^{+}$and $Cu^{2+}$. The sensors were used for a period of four months and their utility has been tested in synthetic and real samples [33].

The best results as silver-selective electrodes were obtained for the PVC membrane based on tetra-(3-hydroxyphenyl) porphyrin which had a working concentration range from $8x10^{-6}$ – $1x10^{-1}$ M. The detection limit of the sensor is $7.0x10^{-6}$ M. The useful pH-range is 5-10. The sensor was used for the determination of chlorides in meat by potentiometric titration.

The sensor having a membrane based on tetra-(3,4-dimetoxyphenyl) could be used in the same pH range as a copper-selective electrode with a working concentration range of $2.5x10^{-6}$ M – $1x10^{-1}$ M, a slope of 27.8 mV/decade copper, a detection limit of $2x10^{-6}$ M and a moderate selectivity over the other tested cations. The sensor was used for the determination of copper from synthetic samples. The AFM of the two membrane electrodes based on porphyrins reveal differences regarding their uniformity of structure and porosity (Figure **5**). Both membranes topography reveal spongeous structures that afford the metal ions to interfere and coordinate with porphyrin both at the surface of membranes and deep into the pores.

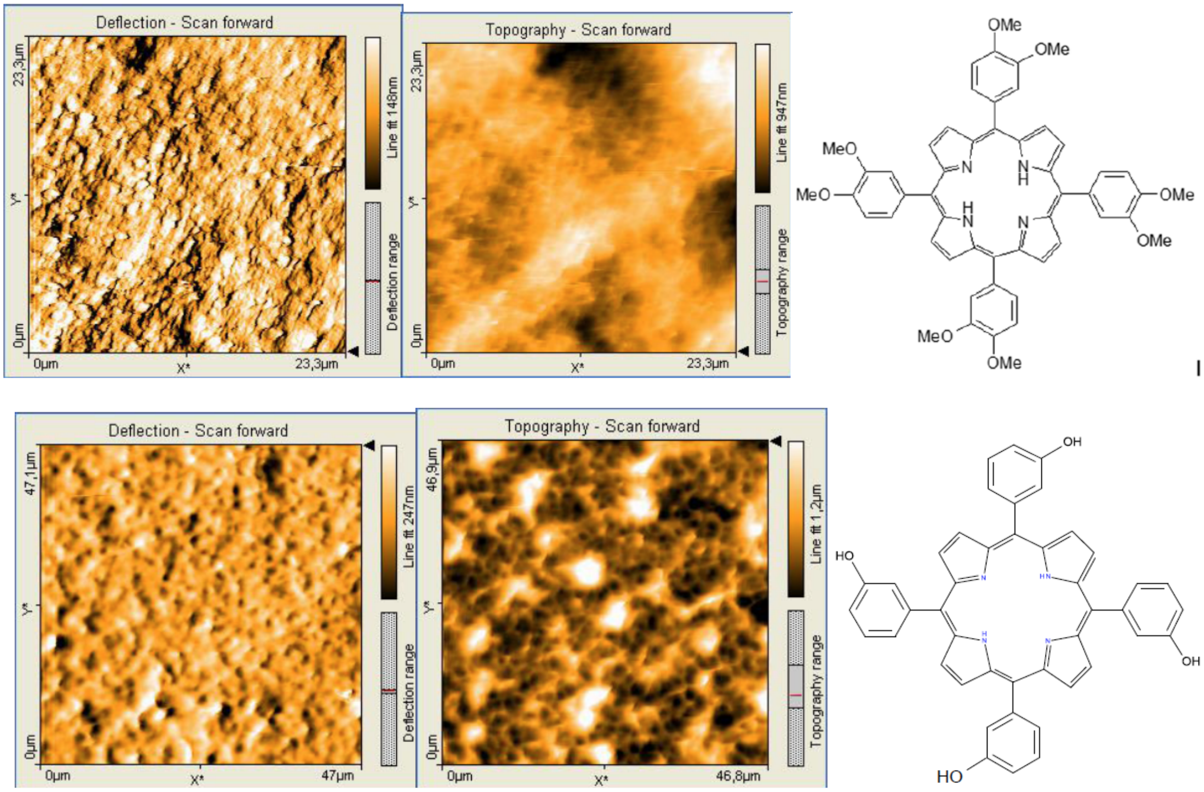

**Figure 5:** AFM images of PVC-membranes with 5, 10, 15, 20-tetrakis(3,4-dimethoxyphenyl) porphyrin and 5, 10, 15, 20-tetrakis(3-hydroxyphenyl)porphyrin.

Copper represents an essential trace element that is recognized for its tremendous necessity in industry, environment and biological systems. The great advantage of ion-selective sensors in comparison with other proposed techniques is that they are measuring the free metal ion activity which is responsible for their toxicity. A symmetrically substituted *meso*-porphyrin 5,10,15,20-tetrakis(4-allyloxyphenyl)porphyrin (Figure **6**) was used as ionophore for a new copper selective-sensor and was also tested for the removal of copper from waste waters. The AFM image revealed the uniform sizes of ring disposition of the porphyrin aggregates in the membrane, realized by successive H and J-types of self-assembling processes.

The best results were obtained for the membrane plasticized with dioctylphthalate. The sensor has linear response in the range $1x10^{-7}$ – $1x10^{-1}$ M with 28.4 ± 0.4

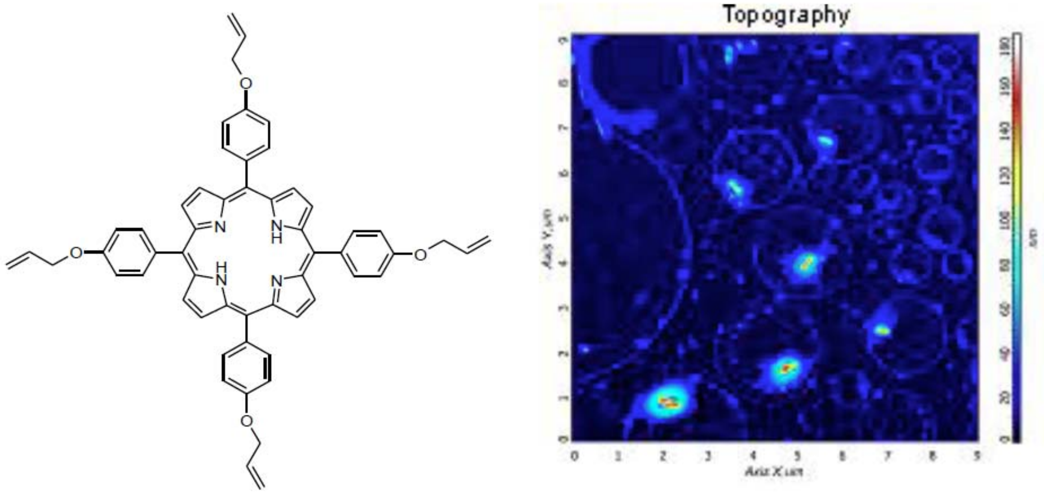

**Figure 6:** The Structure and AFM image of 5,10,15,20-tetrakis(4-allyloxyphenyl)porphyrin.

mV/decade near-Nernstian slope towards copper ions and presents good selectivity. The retention of copper from synthetic copper samples reveals a maximum adsorption capacity of 280 mg/g [37].

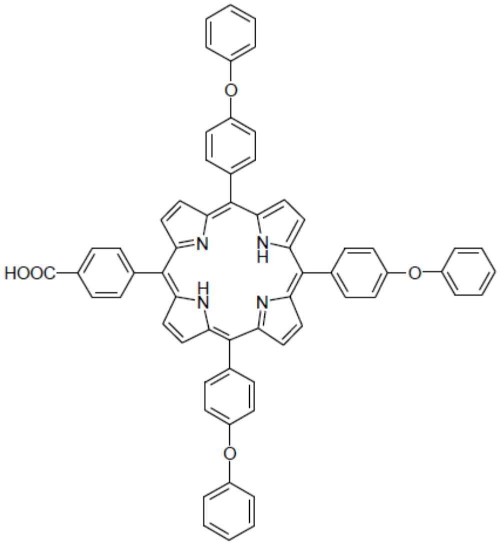

**Figure 7:** The chemical structure of 5-(4-carboxyphenyl)-10,15,20-tris(4-phenoxyphenyl)-porphyrin.

Mixed carboxy-, phenoxy-, pyridyl- and dimethoxy-functionalized $A_3B$ porphyrins were used as ionophores for formulation of PVC-based membrane sensors selective to iron (III). The best results were obtained for the membrane incorporating 5-(4-carboxyphenyl)-10,15,20-tris(4-phenoxyphenyl)-porphyrin (Figure **7**) plasticized with *bis*(2-ethylhexyl)sebacate, in a linear range from $1 \times 10^{-7}$–$1 \times 10^{-1}$ M with a slope of 21.6 mV/decade. The electrode showed high selectivity with respect to alkaline and heavy metal ions and a response time of 20 s. The sensor was tested for the quantitative determination of Fe (III) in recovered solutions from spent lithium ion batteries [38].

The authors presume that the good results are based on the uniform morphology of the membranes. The AFM images registered after deposition of 5-(4-carboxyphenyl)-10,15,20-tris(4-phenoxyphenyl)-porphyrin on silica plates (from a THF solution) displayed the self-assembling architectures of porphyrin at the air - THF interface. Van der Waalsforcesor hydrophobic ones, potential hydrogen bond and π- π stacking got rise tomulti lamellar triangles, uniformly in shape, dimensions (in the range of 350 to 400 nm) and orientation (2D AFM images, Figure **8**). The topography revealed structured channels of deep pores.

### 3.3. Protein Sensors

Conjugated polymers grafted with fluorescent dyes offer the required optical properties for protein sensing, which is an important aspect for many diseases diagnosis. Recently a Zn-metalloporphyrin grafted to a fluorine-phenylene unit with pendant mannose linkages was synthesized by click chemistry methods and Suzuki polymerization. Concanavalin A was colorimetric detected by changes of color from blue to purple [39].

A pyrazine-imprinted polymer and a 1,5-naphthyridine-imprinted polymer, which possess binding sites consisting of two face-to-face porphyrins, (5,10,15,20-tetrakis(4-hydroxyphenyl)-21H,23Hporphine and its Zn complex) were reported. By increasing ofthe pyrazine concentration the fluorescence intensity of the

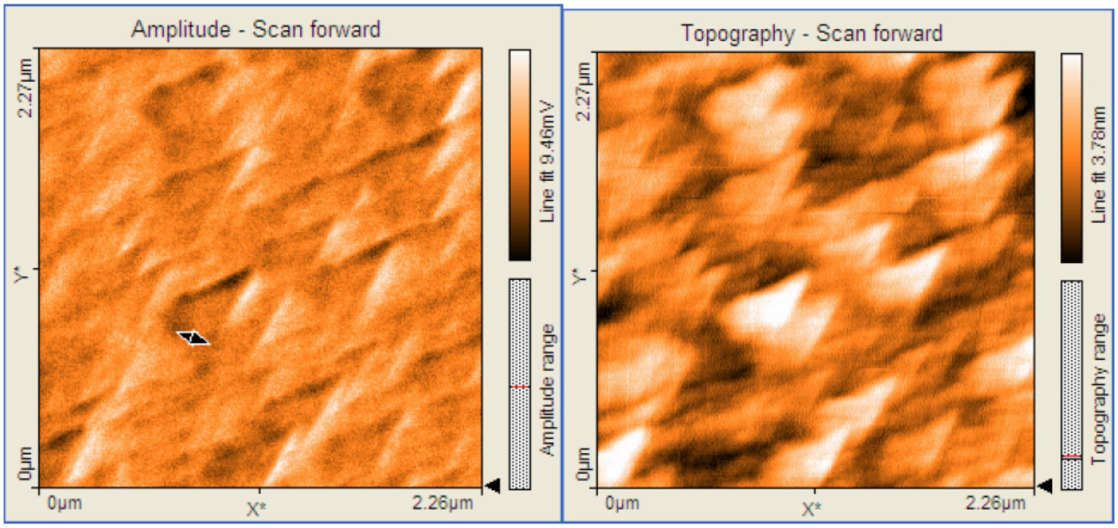

**Figure 8:** 2D AFM image in non-contact mode and topography of multilayered deposition of 5-(4-carboxyphenyl)-10,15,20-tris(4-phenoxyphenyl)-porphyrin.

porphyrin moiety was reduced probably because the coordination bonds between the pyrazine nitrogen and the zinc metal from the porphyrin core. The polymer gave good response to pyrazine in the range of concentrations from 100μM to 10mM, suggesting it is suitable for formulation of a pyrazine sensor [40].

## 4. PORPHYRIN-POLYMER SUBSTRATES ACTING AS CATALYSTS

The metalloporphyrins are acting in catalysis through different oxidationstates of metal centers. The most efficient synthetic porphyrins photosensitizers, that may collect almost 30% of the solar spectrum, are Zn-metalloporphyrins [41].

Based on both the knowledge that iron(III)-metalloporphyrins are acting as biomimetic models of oxidative enzymes (ligninases or peroxidases) being able to catalyze the oxidative degradationof halogenated phenols in the presence of an oxygen donor and the observation that, in a homogeneous system, they suffer rapid self-degradation, many attempts were done to stabilize the catalysts by grafting or immobilizing them on silica hybrids or polymers to obtain reusable catalysts. A water-solubleiron (III)-tetrakis (p-sulfonatephenyl)porphyrin) was tested as catalyst for the oxidation of pentachlorophenol, tetrachlorobisphenol A and tetrabromobisphenol A [42] by forming complexes with cyclodextrin polymers. The performances were excellent and show high reusability.

Porphyrins, especially those substituted by $SO_3H$, COOH or OR groups possess the required properties to be used as photosensitizes for the photoinduced generation of $H_2$, from a sacrificial system [43]. The main requirements [44] for a photosensitizer are: to widely absorb of the incident light, through-out the visible region; to have a good stability in aqueous solution; high efficiency regarding separated ion products upon irradiation in the presence of an electron donor or acceptor and to have a high triplet yield.

Regarding the use of porphyrins as hydrogen evolving catalysts, it was concluded that the catalysts having more negative reduction potentials (porphyrin macrocycle substituted with electron withdrawing groups) can act in the presence of weak acids such as benzoic acid, whereas metalloporphyrins (with macrocycle substituted with inductive donor electron groups) possessing the least negative reduction potentials need stronger acid such as TFA to promote hydrogen evolution [43]. Pyridylmeso-substituted Co-metalloporphyrins co-polymerized in the presence of p-xylil and Nafion gave some promising results for producing of hydrogen [45].

Advances have been made also by using water-soluble iron (III)-tetrakis (*p*-sulfonatephenyl) porphyrin grafted on cyclodextrin polymers for the oxidation of tetrabromobisphenol at pH 8. The efficiency for oxidative degradation and the reusability were increased in comparison with known catalysts [42].

Palladium(II) complex of *meso*-tetra(*p*-hydroxy-phenyl)porphyrin was grafted on cross-linked chloro-methylated polystyrene and tested as novel Heck reaction catalyst [46]. The polystyrene-functionalized metalloporphyrin-complex was an efficient heterogeneous catalyst for cross-coupling of aryl iodides with ethyl acrylate with high efficiency of 99.8%. The catalyst can be reused several times, preserving its catalytic activity.

A new tetraphenylporphyrin-heteropoly acid hybrid was applied in Baeyer–Villiger oxidation of cyclohexanone to caprolactone with molecular oxygen [47].

## 5. PHOTOACTIVE PORPHYRIN-POLYMERS FOR SOLAR CELLS-RECENT DEVELOPMENTS

Polymer based materials are a benefit for solar cells construction due to their unique advantages, such as low cost, light weight and flexibility of architecture (usually the structure is formed from a photoactive layer of a conjugated polymer donor and a fullerene derivative acceptor, sandwiched between an anode and a cathode, but the recent advances described multiple-junction tandem solar cell [48] and ternary solar cells [49].

Novel ordered porous films have found applications in the fields of photonic crystals and solar cells [50]. Recently, honeycomb-patterned films obtained by self-assembly of polystyrene with poly (ethylene glycol) incorporating meso-tetra (N-methy-4-pyridyl) porphinetetratosylate in the presence of diisooctyl sodium sulfosuccinate showed the desired fluorescent properties due to the porphyrin preserved optical properties [51].

Due to the importance of excitonic coupling between chromophores, that has a principal role in migration processes of singlet and triplet excited states, polycyclobutene bearing zinc porphyrin as a pendant group was subjected for the study of these excitonic states [52].

Increasing of photo conversion efficiency is the main purpose in formulation of solar cells, so the donor-acceptor pairs are carefully designed. Recently two new conjugated acceptor–donor–acceptor (A–π-D–π-A) compounds having a Zn-porphyrin acting as donor and linked by ethynylenes to one or two units of thienylenevinylene and capped by dicyanovinylene groups as acceptor units have been obtained and their photophysical properties were investigated [53].

A novel solar cell made of polythiophene containing a 25% molar content of porphyrin sensitizer dye as the active layer, exhibits higher power conversion efficiency, short circuit current and fill factor values better than the reference cell based on polythiophene completely devoid of porphyrin [54].

## 6. POLYMER-PORPHYRIN HYBRID-SYSTEMS IN MEDICINE

### 6.1. Recent Drug Delivery Systems Based on Polymer-Porphyrin

During the last decade, the strategy consisting in co-delivery of drugs and gene [55, 56] modified the methods used in cancer therapy because this approach might develop synergistic effects, enhance selectivity towards targeted cells and eliminate the drawbacks related to drug resistance.

Thus, a star-shaped copolymer consisting of a carboxy-functionalized porphyrin core with photochemical internalization effect and arginine functionalized poly (L-lysine) dendron arms has been designed, and used to codeliver docetaxel (DOC) and MMP-9 shRNA plasmid for nasopharyngeal cancer therapy.

This complex system induced a more significant apoptosis than DOC or MMP-9 used alone and proved to be non-toxic [57]. The optimum ratio between drug and gene is still in testing.

Manganese-porphyrin conjugated onto the surface of doxorubicin-loaded poly (lactic acid) show capabilities for magnetic resonance imaging and pH-sensitive drug delivery [58].

A novel hybrid amphiphilic polymer comprising polyethylene glycol, poly (d, l-lactide-co-glycolide) and porphyrin showed the capacity to accumulate in the tumor and to be internalized by tumor cells for drug release in acidic organelles. The porphyrin-polymer micelles can be simultaneously loaded with two chemotherapeutic drugs showing synergistic cytotoxicity towards triple-negative breast cancer, that is a malignant cancer type [59].

### 6.2. Antibacterial Activity of Porphyrin-Polymer Hybrids

Series of porphyrinic photosensitizers, namely: 5-[4-(3-ethoxycarbonylpropyloxy)phenyl]-10,15,20-tri(4-methylphenyl) porphyrin, 5-[4-(10-methoxycarbonyldecan-oxy)-phenyl]-10,15,20- tri(4-methylphenyl) porphyrin, 5-[4-(3-carboxypropyloxy)phenyl]-10,15,20-tri(4-methyl-phenyl) porphyrin and 5-[4-(10-carboxydecanoxy) phenyl]-10,15,20-tri(4-methylphenyl) porphyrin, that are covalently linked to the cellulose laurate esterspolymer were obtained by using two-steps esterification reaction [60]. The photobactericidal activity of these porphyrn – polymer materials was evaluated against Gram positive and Gram negative strains bacteria (*E. coli* and *S. aureus*.). Photobactericidal activity is exhibited if porphyrin grafting percentage is higher than 0.16. If porphyrin is not present, the material allowed full growth of bacteria. These materials represent an alternative to antibiotics in order to overcome the growing bacterial multiresistance.

Platinum nanoparticles of different shapes and sizes were conjugated by active carbodiimide ester groups with ClGa (III) 5,10,15,20-tetrakis-(4-carboxyphenyl) porphyrin. These conjugates were used for photodynamic antimicrobial chemotherapy against Staphylococcus aureus using fluences ranged from 0 to 5 J cm$^{-2}$ at an irradiance of 0.05Wcm$^{-2}$ and as a result 99.9% of the bacteria have been killed [61].

Grafting a neutral porphyrin, the metallated 5-(4-azidophenyl)-10,15,20-triphenylporphyrin, onto ligno-cellulosic fibers by cycloaddition reaction, gave a material with antimicrobial activity, that was tested under visible light irradiation with a low light dose (9.5 J/cm2) against two pathogenic bacterial strains, namely: Gram (+) *Staphylococcus aureus* and Gram (−) *Pseudomonas aeruginosa*.

The authors demonstrated [62] that type II photochemical pathway, in which photosensitizer transfers its energy to molecular oxygen is responsible for the photoinactivation of cells.

The singlet oxygen formed *in situ* reacts rapidly with its biological environment and produces injuries, apoptosis or the death of microorganisms. Another explanation [63] is that the photosensitizer does not need to penetrate the bacteria in order to be effective.

### 6.3. Polymer-Porphyrins Photoactive in PDT

The non-invasive method Photodynamic therapy of cancer (PDT) is based on photochemical interactions between photosensitizers (PS) and molecular oxygen under light irradiation with broadband red light [64].

Although porphyrins provide selective accumulation in malignant tissues, selectivelocalization of light irradiation and relatively fastelimination from the body, due to their hydrophobic properties, they bring drawbacks such as self-quenching and photo-toxicity to the skin. Polymer functionalization of porphyrin is commonly used to overcome some of these inconveniences [65].

A set of nineteen $A_2B_2$, $A_2BC$ and $A_3B$ porphyrins mixed substituted with different donor and acceptor groups were studied by pulse train fluorescence technique, revealing that porphyrins substituted with methoxyphenyl groups are prospective photosensitizing candidates to be tested in photodynamic therapy of cancer and in light harvesting processes [66].

An $A_3B$ mixed substituted cationic porphyrin 5,10,15-triphenyl-20-(3-N-methylpyridinium-yl)porphyrin encapsulated in marine atelocollagen/xanthane gum microcapsules [67] of about 300–400 nm, provided enhanced photodynamic activity. The polymeric – porphyrin hybrid was more phototoxic towards HeLa cells than the phosphatidylcholine lipidic emulsion, demonstrating its potential use for photodynamic therapy of cancer.

Star-shaped porphyrin-cored poly(L-lactide)-block-poly(N-isopropylacrylamide) copolymer transformed in aqueous solution from spherical micelles through wormlike micelles to vesicles, and the lower critical solution temperatures were 37.9°, 37.2°, 35.9°, respectively. The *in vitro* study showed apparent phototoxicity toward BEL-7402 cancer cells [68].

Another star-like polymer comprising of porphyrin core, gadolinium chelate and poly-ethylenglycole displayed strong red fluorescence when excited at 585 nm. The *in vivo* MRI and *ex vivo* fluorescent imaging experiments indicated that the probe had excellent tumor-targeting capability [69].

Triblock copolymers of ethylene- and propylene oxide – Pluronics® functionalized with porphyrin exhibit enhanced photosensitizing activity in the generation of singlet oxygen in aqueous media in comparison with pure porphyrins. All Pluronics form similar dendritic structures independently of their molecular weight and degree of hydrophobicity. Authors [70] concluded that porphyrin aggregates interact with the hydrophobic groups of Pluronics determining the polymer chains to cover porphyrin-containing units. These interactions produced the encapsulation of porphyrins aggregates inside a Pluronic micelle.

### 6.4. Fluorescence Imaging Based on Porphyrin Functionalized Polymers

Fluorescence imaging is a non-invasive imaging technique with wide potential for the investigation of biomaterials *in vivo*, due to its high sensitivity and low-energy radiation.

Porphyrin functionalized polymers preserving the optical properties of porphyrin show the requested stability to be used in bioimaging and drug delivery.

A star PEG–PCL copolymer with porphyrin core, in the form of hydrogel provided useful fluorescence for *in vivo* applications such visualization and a drug carrier for monitoring drug delivery [71].

Other types of red light-emitting star polymers, based on zinc 5,10,15,20-tetrakis(4-(2-methyl-2-bromopropoxy)phenyl) porphyrin were prepared *via* atom transfer radical polymerization using 9-(4-vinylbenzyl)-9H-carbazole and methacrylate-type monomer 2-(9Hcarbazole-9-yl)-ethyl methacrylate. The grafting of fluorescent red porphyrin dye into the blue light-emitting polymers might generate efficient transfer of energy from blue to red [72].

Porphyrin-polyethylene glycol diamines can serve as effective multimodal markers of renal function, because they possess fluorescence imaging properties.

Besides, these structures can be used for monitoring of oxygen concentration. Porphyrins and tetrapyrrolic derivatives have long been used as theranostic agents [73]. In this respect, polymeric-porphyrin materials have been synthesized by cross-linking of tetra-functionalized porphyrins with bifunctional linkers.

Polyethylene glycol diamines can crosslink meso-tetra(4-carboxyphenyl) porphyrin to form a fully insoluble hydrogel, that is also biocompatible to be used *in vivo* biosensing applications as a multimodal marker for renal function [74].

Star polymers-based on porphyrin core exhibit enhanced thermal stability properties and red light emission in the solid state making them promising materials for optical devices [72]. It is known that aggregation is accompanied by quenching of fluorescence in the solid state and the flexible arms of the star polymer can effectively hinder π-π interactions, preventing in this way H –type aggregation, between porphyrin macrocycles. In this way the emission properties will be preserved.

## RELATED EXPERIMENTAL ISSUES

AFM imaging was carried out on Nanosurf® Easy Scan 2 Advanced Research microscope. The samples were obtained by drop casting on silica plates and all AFM images belong to original and unpublished results of the authors.

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## REFERENCES

[1] Ishihara S, Labuta J, Van Rossom W, *et al*. Porphyrin-based sensor nanoarchitectonics in diverse physical detection modes. Phys Chem Chem Phys 2014; 16: 9713-46. http://dx.doi.org/10.1039/c3cp55431g

[2] Basu J, Rohatgi-Mukherjee KK. Photoelectrochemical characterisation of porphyrin-coated electrodes. Sol Energy Mater1991; 21: 317-25. http://dx.doi.org/10.1016/0165-1633(91)90029-K

[3] Basu BJ. Optical oxygen sensing based on luminescence quenching of platinum porphyrin dyes doped in ORMOSIL coatings. Sensor Actuat B-Chem 2007; 123: 568-77. http://dx.doi.org/10.1016/j.snb.2006.09.062

[4] Wang T, SheY, Fu H, Li H. Selective cyclohexane oxidation catalyzed by manganese porphyrins and co-catalysts. Catal Today 2016; 264: 185-90. http://dx.doi.org/10.1016/j.cattod.2015.07.034

[5] Kowalewska B, Skunik M, Karnicka K, *et al*. Enhancement of bio-electrocatalytic oxygen reduction at the composite film of cobalt porphyrin immobilized within the carbon nanotube-supported peroxidase enzyme. Electrochim Acta 2008; 53: 2408-15. http://dx.doi.org/10.1016/j.electacta.2007.10.005

[6] Hu X, Tang K, Liu SG, Zhang YY, Zou GL. Hemoglobin-biocatalysts synthesis of a conducting polyaniline. React Funct Polym 2005; 65: 239-48. http://dx.doi.org/10.1016/j.reactfunctpolym.2005.06.007

[7] Shi J, Liu TWB, Chen J, *et al*. Transforming a targeted porphyrin theranostic agent into a PET imaging probe for cancer. Theranostics 2011; 1: 363-70. http://dx.doi.org/10.7150/thno/v01p0363

[8] Deda DK, Budu A, Cruz LN, Araki K, Garcia CRS. Strategies for development of antimalarials based on encapsulated porphyrin derivatives. Mini Rev Med Chem 2014; 14: 1055-71. http://dx.doi.org/10.2174/1389557515666150101094829

[9] Baldea I, Olteanu DE, Bolfa P, *et al*. Efficiency of photodynamic therapy on WM35 melanoma with synthetic porphyrins: role of chemical structure, intracellular targeting and antioxidant defense. J Photoch Photobiol B2015; 151: 142-52.

[10] Tauskela JS, Brunette E, Hewitt M, Mealing G, Morley P. Competing approaches to excitotoxic neuroprotection by inert and catalytic antioxidant porphyrins. Neurosci Lett 2006; 401: 236-41. http://dx.doi.org/10.1016/j.neulet.2006.03.046

[11] Harmon HJ, Oliver A. Optical biodetection using receptors and enzymes (porphyrin-incorporated). In: Schaudies RP, editor. Biological identification. Elsevier Ltd 2014; p. 253-6. http://dx.doi.org/10.1533/9780857099167.3.253

[12] Giancane G, Valli L. State of art in porphyrin Langmuir–Blodgett films as chemical sensors. Adv Colloid Interfac 2012; 171–172: 17-35. http://dx.doi.org/10.1016/j.cis.2012.01.001

[13] Zhu G, Sun Q, Kawazoe Y, Jena P. Porphyrin-based porous sheet: optoelectronic properties and hydrogen storage. Int J Hydrogen Energ 2015; 40: 3689-96. http://dx.doi.org/10.1016/j.ijhydene.2015.01.069

[14] O'Regan B, Gratzel M. A low-cost, high-efficiency solar cell based on dye-sensitized colloidal $TiO_2$ films. Nature 1991; 353: 737-40. http://dx.doi.org/10.1038/353737a0

[15] da Costa VCP, Hwang BJ, Eggen SE, Wallace MJ, Annunziata O. Formation and thermodynamic stability of (polymer + porphyrin)supramolecular structures in aqueous solutions. J Chem Thermodyn 2014; 75: 119-27. http://dx.doi.org/10.1016/j.jct.2014.02.025

[16] El-Bindary AA, El-Sonbati AZ, Diaba MA, Ghoneim MM, Serag LS, Polymeric complexes — LXII. Coordination chemistry of supramolecular Schiff base polymer complexes. J Mol Liq 2016; 216: 318-29. http://dx.doi.org/10.1016/j.molliq.2015.12.113

[17] Taniguchin I, Kinugasa K, Egashira S, Higa M. Preparation of well-defined hyper-branched polymers and the $CO_2$ separation performance and storage of gases. J Membr Sci 2016; 502: 124-32. http://dx.doi.org/10.1016/j.memsci.2015.12.032

[18] Ikeda A, Hatano T, Shinkai S, Akiyama T, Yamada S. Efficient photocurrent generation in novel self assembled multilayers comprised of [60]fullerene–cationic homooxacalix[3]arene inclusion complex and anionic porphyrin polymer. J Am Chem Soc 2001; 123: 4855-6. http://dx.doi.org/10.1021/ja015596k

[19] Takechi K, Shiga T, Motohiro T, *et al*. Solar cells using iodine-doped polythiophene–porphyrin polymer films. Sol Energ Mat Sol C 2006; 90: 1322-30. http://dx.doi.org/10.1016/j.solmat.2005.08.010

[20] Vlascici D, Pica EM, Cosma V, Fagadar-Cosma E. Potentiometric characterization of lead-selective electrodes based on a phenyl disubstituted porphyrin. J Porphyr Phthalocya 2008; 12: 772.

[21] Grama S, Hurduc N, Fagadar-Cosma E, Vasile M, Tarabukina E, Fagadar-Cosma G. Novel porphyrin-based polysiloxanemicro material. Dig J Nanomater Bios 2010; 5: 959-73.

[22] Itagaki Y, Nakashima S, Sadaoka Y. Optical humidity sensor using porphyrin immobilized Nafion composite films. Sensor Actuat B-Chem2009; 142: 44-8. http://dx.doi.org/10.1016/j.snb.2009.07.033

[23] Wang L, Meyerhoff ME. Polymethacrylate polymers with appended aluminum (III)-tetraphenylporphyrins: synthesis, characterization and evaluation as macromolecular ionophores for electrochemical and optical fluoride sensors. Anal Chim Acta 2008; 611: 97-102. http://dx.doi.org/10.1016/j.aca.2008.01.070

[24] Liu MH, Su YO. Electrocatalytic reactions by an iron porphyrin/polypyrrole modified electrode monitored by electrochemical quartz crystal microbalance. J Chin ChemSoc-Taip1999; 46: 115-9.
http://dx.doi.org/10.1002/jccs.199900015

[25] Fagadar-Cosma E, Tarabukina E, Zakharova N, *et al*. Hybrids formed between polyvinylpyrrolidone and an $A_3B$ porphyrin dye: behavior in aqueous solutions and chemical response to $CO_2$ presence. Polym Int 2016; 65: 200-9.
http://dx.doi.org/10.1002/pi.5047

[26] Poriel C, Ferrand Y, Le Maux P, Paul-Roth C, Simonneaux G, Rault-Berthelot J. Anodic oxidation and physicochemical properties of various porphyrin-fluorenes or -spirobifluorenes: Synthesis ofnew polymers for heterogeneous catalytic reactions. J Electroanal Chem 2005; 583: 92-103.
http://dx.doi.org/10.1016/j.jelechem.2005.05.005

[27] Birdeanu M, Fagadar-Cosma E. The self-assembly of porphyrin derivatives into 2D and 3D architectures. In:Putz M, editor. Quantum nanosystems: structure, properties and interactions. Toronto-New Jersey: Apple Academics Press 2014: p. 173-206.
http://dx.doi.org/10.1201/b17412-6

[28] Drain CM, Varotto A, Radivojevic I. Self-organized porphyrinic materials. Chem Rev 2009; 109: 1630-58.
http://dx.doi.org/10.1021/cr8002483

[29] Guo L. Side-chain-controlled H- and J-aggregation of amphiphilic porphyrins in CTAB micelles. J Colloid Interf Sci 2008; 322: 281-6.
http://dx.doi.org/10.1016/j.jcis.2008.02.041

[30] Fagadar-Cosma E, Fagadar-Cosma G, Vasile M, Enache C. Synthesis, spectroscopic and self-assembling characterization of novel photoactive mixed aryl-substituted porphyrin. Curr Org Chem 2012; 16: 931-41.
http://dx.doi.org/10.2174/138527212800194755

[31] Zhang Z, Li X, Zhao Q, *et al*. Facile synthesis and characterizations of copper–zinc-10,15,20-tetra(4-pyridyl) porphyrin (Cu–ZnTPyP) coordination polymer with hexagonal micro-lump and micro-prism morphologies. J Colloid Interf Sci 2014; 432: 229-35.
http://dx.doi.org/10.1016/j.jcis.2014.07.005

[32] Rieter WJ, Pott KM, Taylor KML, Lin W. Nanoscale coordination polymers for platinum-based anticancer drug delivery. J Am Chem Soc 2008; 130: 11584-5.
http://dx.doi.org/10.1021/ja803383k

[33] Vlascici D, Fagadar-Cosma E, Pica EM, Cosma V, Bizerea O, Mihailescu G, Olenic L. Free base porphyrins as ionophores for heavy metal sensors. Sensors 2008; 8: 4995-5004.
http://dx.doi.org/10.3390/s8084995

[34] Monti D, Nardis S, Stefanelli M, Paolesse R, Di Natale C, D'Amico A. Porphyrin-based nanostructures for sensing applications. J Sensors 2009; 2009: 10 pages.
http://dx.doi.org/10.1155/2009/856053

[35] Evyapan M, Dunbar ADF. Controlling surface adsorption to enhance the selectivity of porphyrinbased gas sensors. Appl Surf Sci 2016; 362: 191-201.
http://dx.doi.org/10.1016/j.apsusc.2015.11.210

[36] Wang Y, Wu F. Amphiphilic acrylamide-based copolymer with porphyrin pendants for the highly selective detection of $Hg^{2+}$ in aqueous solutions. Polymer 2015; 56: 223-8.
http://dx.doi.org/10.1016/j.polymer.2014.11.037

[37] Vlascici D, Popa I, Chiriac VA, Fagadar-Cosma G, Popovici H, Fagadar-Cosma E. Potentiometric detection and removal of copper using porphyrins. Chem Cent J 2013; 7: 111-8.
http://dx.doi.org/10.1186/1752-153X-7-111

[38] Vlascici D, Fagadar-Cosma E, Popa I, Vlad Chiriac V, Gil-Agusti M. A novel sensor for monitoring of iron (III) ions based on porphyrins. Sensors 2012; 12: 8193-203.
http://dx.doi.org/10.3390/s120608193

[39] Wang L, Fang G, Li L, Cao D. Synthesis, characterization and detection of Concanavalin A based on a mannose-substituted conjugated polymer through aggregation-enhanced FRET. Sensor Actuat B-Chem 2016; 229: 47-56.
http://dx.doi.org/10.1016/j.snb.2016.01.111

[40] Matsui J, Sodeyama T, Saiki Y, *et al*. Face-to-face porphyrin moieties assembled with spacing for pyrazine recognition in molecularly imprinted polymers. Biosens Bioelectron 2009; 25: 635-9.
http://dx.doi.org/10.1016/j.bios.2009.01.047

[41] Harriman A, Porter G, Richoux MC.P hotosensitised reduction of water to hydrogen using water-soluble zinc porphyrins. J ChemSoc Farad T 21981; 77: 833-44.

[42] Miyamoto T, Zhu Q, Igrashi M, Kodama R, Maeno S, Fukushima M. Catalytic oxidation of tetrabromobisphenol A byiron(III)-tetrakis(p-sulfonatephenyl)porphyrin catalyst supported oncyclodextrin polymers with potassium monopersulfate. J Mol Catal B-Enzym 2015; 119: 64-70.
http://dx.doi.org/10.1016/j.molcatb.2015.06.002

[43] Ladomenou K, Natali M, Iengo E, Charalampidis G, Scandola F, Coutsolelos AG. Photochemical hydrogen generation with porphyrin-based systems. Coord Chem Rev 2015; 304-305: 38-54.
http://dx.doi.org/10.1016/j.ccr.2014.10.001

[44] Harriman A, Porter G. Photochemistry of manganese porphyrins. J Chem Soc Farad T 2 1979; 75: 1532-42.
http://dx.doi.org/10.1039/F29797501532

[45] Kellett RM, Spiro TG. Cobalt (I) porphyrin catalysis of hydrogen production from water. Inorg Chem 1985; 24: 2378-82.
http://dx.doi.org/10.1021/ic00209a012

[46] Huang Y, Yang L, Huang M, *et al*. Polystyrene microsphere-immobilized palladium(II) porphyrin as mild, reusable, and highly efficient catalyst for Heck reaction. Particuology 2015; 22: 128-33.
http://dx.doi.org/10.1016/j.partic.2014.08.003

[47] Pamin K, Prończuk M, Basąg S, Kubiak W, Sojka Z, Połtowicz J. A new hybrid porphyrin-heteropolyacid material: Synthesis, characterization and investigation as catalyst in Baeyer–Villiger oxidation. Synergistic effect. Inorg Chem Commun 2015; 59: 13-6.
http://dx.doi.org/10.1016/j.inoche.2015.06.005

[48] Chang CY, Zuo L, Yip HL, *et al*. A versatile fluoro-containing low-band gap polymer for efficient semitransparent and tandem polymer solar cells. Adv Funct Mater 2013; 23: 5084-90.
http://dx.doi.org/10.1002/adfm201301557

[49] Yusoff ARBM, Kim D, Kim H P, Shneider F K, Da Silva WJ, Jang J. A high efficiency solution processed polymer inverted triple-junction solar cell exhibiting a power conversion efficiency of 11.83%. Energy Environ Sci 2015; 8: 303-16.
http://dx.doi.org/10.1039/C4EE03048F

[50] Kwak ES, Lee W, Park NG, Kim J, Lee H. Compact inverse-opal electrode using non-aggregated $TiO_2$ nanoparticles for dye-sensitized solar cells. Adv Funct Mater 2009; 19: 1093-9.
http://dx.doi.org/10.1002/adfm.200801540

[51] Fan D, Xia X, Ma H, Du B, Wei Q. Honeycomb-patterned fluorescent films fabricated by self-assembly of surfactant-assisted porphyrin/polymer composites. J Colloid Interf Sci 2013; 402: 146-50.
http://dx.doi.org/10.1016/j.jcis.2013.03.030

[52] Fujitsuka M, Satyanarayana K, Luh TY, Majima T. Singlet–singlet and singlet–triplet annihilations in structure-regulated porphyrin polymers. J Photochem Photobiol A Chem 2015.
http://dx.doi.org/10.1016/j.jphotochem.2015.10.011

[53] Arrechea S, Molina-Ontoria A, Aljarilla A, de la Cruz P, Langa F, Echegoyen L. New acceptor–π-porphyrin–π-acceptor systems for solution-processed small molecule organic solar cells. Dyes Pigments 2015; 121: 109-17.
http://dx.doi.org/10.1016/j.dyepig.2015.04.037

[54] Angiolini L, Benelli T, Cocchi V, Lanzi M, Salatelli E. Side chain porphyrin moiety linked to polymer-fullerene composite solar cell. React Funct Polym 2013; 73: 1198-206. http://dx.doi.org/10.1016/j.reactfunctpolym.2013.05.007

[55] Han K, Chen S, Chen WH, *et al*. Synergistic gene and drug tumor therapy using a chimeric peptide. Biomaterials 2013; 34: 4680-9. http://dx.doi.org/10.1016/j.biomaterials.2013.03.010

[56] Ma D, Zhao Y, Zhou XY, *et al*. Photoenhanced gene transfection by a star-shaped polymer consisting of a porphyrin core and poly(L-lysine) dendron arms. Macromol Biosci 2013; 13: 1221-7. http://dx.doi.org/10.1002/mabi.201300139

[57] Ma D, Lin QM, Zhang LM, Liang YY, Xue W. A star-shaped porphyrin-arginine functionalized poly(L-lysine) copolymer for photo-enhanced drug and gene co-delivery. Biomaterials 2014; 35: 4357-67. http://dx.doi.org/10.1016/j.biomaterials.2014.01.070

[58] Jing L, Liang X, Li X, Yang Y, Dai Z. Covalent attachment of Mn-porphyrin onto doxorubicin-loaded poly(lactic acid) nanoparticles for potential magnetic resonance imaging and pH-sensitive drug delivery. Acta Biomater 2013; 9: 9434-41. http://dx.doi.org/10.1016/j.actbio.2013.08.018

[59] Su S, Ding Y, Li Y, Wu Y, Nie G. Integration of photothermal therapy and synergistic chemotherapy by a porphyrin self-assembled micelle confers chemosensitivity in triple-negative breast cancer. Biomaterials 2016; 80: 169-78. http://dx.doi.org/10.1016/j.biomaterials.2015.11.058

[60] Krouit M, Granet R, Krausz P. Photobactericidal films from porphyrins grafted to alkylated cellulose – synthesis and bactericidal properties. Eur Polym J 2009; 45: 1250-9. http://dx.doi.org/10.1016/j.eurpolymj.2008.11.036

[61] Managa M, Nyokong T. Photodynamic antimicrobial chemotherapy activity of gallium tetra-(4-carboxyphenyl) porphyrin when conjugated to differently shaped platinum nanoparticles. J Mol Struct 2015; 1099: 432-40. http://dx.doi.org/10.1016/j.molstruc.2015.06.077

[62] TaKeki JKN, Ouk TS, Zerrouki R, Faugeras PA, Sol V, Brouillette F. Synthesis and photobactericidal properties of a neutral porphyrin grafted onto lignocellulosic fibers. Mat Sci Eng C 2016; 62: 61-7. http://dx.doi.org/10.1016/j.msec.2016.01.028

[63] Dahl TA, Midden WR, Hartman PE. Comparison of killing of gram-negative and gram-positive bacteria by pure singlet oxygen. J Bacteriol 1989; 171: 2188-94.

[64] Zhang GD, Harada A, Nishiyama N, *et al*. Polyion complex micelles entrapping cationic dendrimerporphyrin: effective photosensitizer for photodynamic therapy of cancer. J Control Release 2003; 93: 141-50. http://dx.doi.org/10.1016/j.jconrel.2003.05.002

[65] Dai XH, Wang ZM, Gao LY, *et al*. Starshaped poly(L-lactide)-b-poly(ethylene glycol) with porphyrin core: synthesis, self-assembly, drug-release behavior and singlet oxygen research. New J Chem 2014; 38: 3569-78. http://dx.doi.org/10.1039/C3NJ01621H

[66] De Souza TGB, Vivas MG, Mendonça CR, *et al*. Studying the intersystem crossing rate and triplet quantum yield of meso-substituted porphyrins by means of pulse train fluorescence technique. J Porphyrins Phthalocyanines 2016. http://dx.doi.org/10.1142/S1088424616500048

[67] Deda DK, Uchoa AF, Caritá E, Baptista MS, Toma HE, Araki K. A new micro/nanoencapsulated porphyrin formulation for PDT treatment. Int J Pharm 2009; 376: 76-83. http://dx.doi.org/10.1016/j.ijpharm.2009.04.024

[68] Dai XH, Jin H, Cai MH, *et al*. Fabrication of thermosensitive, star-shaped poly(L-lactide)-block-poly(N-isopropylacrylamide) copolymers with porphyrin core for photodynamic therapy. React Funct Polym 2015; 89: 9-17. http://dx.doi.org/10.1016/j.reactfunctpolym.2015.02.002

[69] Hu H, Sheng Y, Ye M, Qian Y, Tang J, Shen Y. A porphyrin-based magnetic and fluorescent dual-modal nanoprobe for tumor imaging. Polymer 2016; 88: 94-101. http://dx.doi.org/10.1016/j.polymer.2016.02.026

[70] Kotova SL, Timofeeva VA, Belkova GV, Aksenova NA, Solovieva AB. Porphyrin effect on the surface morphology of amphiphilic polymers as observed by atomic force microscopy. Micron 2012; 43: 445-9. http://dx.doi.org/10.1016/j.micron.2011.10.025

[71] Dong X, Wei C, Lu L, Liu T, Lv F. Fluorescent nanogel based on four-arm PEG–PCL copolymer with porphyrin core for bioimaging. Mat Sci Eng C 2016; 61: 214-9. http://dx.doi.org/10.1016/j.msec.2015.12.037

[72] Tao Y, Xu Q, Li N, Lu J, Wang L, Xia X. Synthesis and photoluminescent property of star polymers with carbzole pendent and a zinc porphyrin core by ATRP. Polymer 2011; 52: 4261-7. http://dx.doi.org/10.1016/j.polymer.2011.07.025

[73] Zhang Y, Lovell JF. Porphyrins as theranostic agents from prehistoric to modern times. Theranostics 2012; 2: 905-15. http://dx.doi.org/10.7150/thno.4908

[74] Huang H, Hernandez R, Geng J, *et al*. A porphyrin-PEG polymer with rapid renal clearance. Biomaterials 2016; 76: 25-32. http://dx.doi.org/10.1016/j.biomaterials.2015.10.049

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