ROMANIAN ACADEMY
School of Advanced Studies of the Romanian Academy
"Coriolan Drăgulescu" Institute of Chemistry

PhD Thesis Summary

POSSIBLE INTERFERENCE BETWEEN SYNTHETIC PORPHYRINS AND PLATINUM GROUP METALS. APPLICATIONS IN PLATINUM RECOVERY, SENSORISTICS AND DISCOLORATION OF WASTEWATER

PhD SUPERVISOR:
CS I. Dr. Ing. Eugenia FĂGĂDAR-COSMA

PhD STUDENT:
Frățilescu Ion

2024

Content of the thesis

Keywords: porphyrin derivatives, metalloporphyrins, Pt(II)-porphyrins, optical sensors, fluorimetric sensors, electrochemical sensor, CO_2 sensor, CO_2 capture, platinum recovery, methylene blue removal, basic fuchsin discoloration/removal, TLC, UV-Vis spectroscopy, FT- IR, ^{1}H-NMR. ^{13}C-NMR, SEM microscopy, HRTEM, AFM, BET

Introduction

Porphyrin derivatives represent a fascinating class of chemical compounds with complex structures, which derive from the fundamental porphin molecule (Figure 1). These compounds properties are dictated by the presence of an extended aromatic character, due to extended conjugation. In addition, they possess numerous reaction centres, consisting both in peripheral functional groups and metal cores, which confer a diverse palette of potential applications.

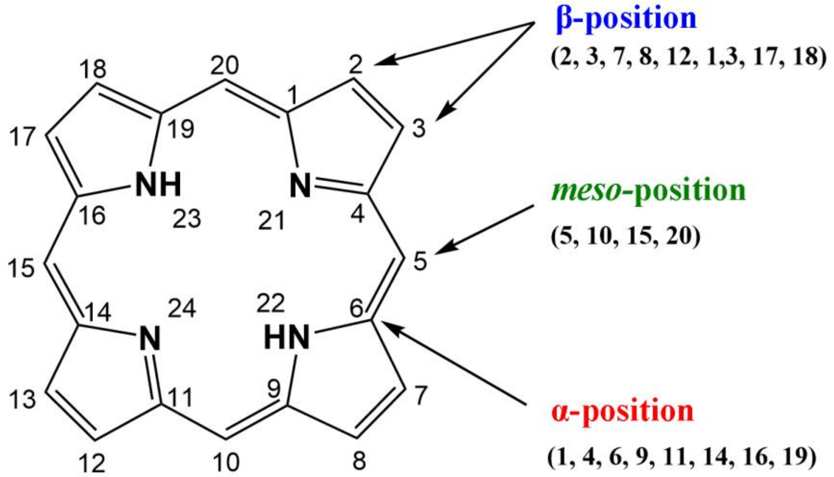

Figure 1. Porphyrin macrocycle structure (porphine structure) and position numbering according to IUPAC nomenclature

A simple and efficient way to obtain these porphyrinic derivatives is the Adler-Longo method. This method involves the condensation of pyrrole with aldehydes in an acidic reactive medium.

An essential aspect in the study and use of porphyrins is their capacity to be metalated. This procedure involves the coordination of a metal ion in the core of the porphyrin. The metalloporphyrins obtained in this way present completely new functionalities.

The applications of metalloporphyrins, including Pt(II)-metalloporphyrins, are extremely varied and significant in a wide range of fields. Notable examples are: asymmetric heterogeneous catalysis [1], hydrogen generation [2], directed organic catalysis [3], molecular transport systems [4] and as photosensitizers in photodynamic cancer therapy [5].

Hybrid or composite nanomaterials containing porphyrin-base or metalloporphyrins have a number of valuable applications that can be extended depending on their targeted morphology and opto-electronic properties, towards the development of gas sensors [6], optical sensors [7], adsorbent materials for CO_2 storage [8] or for discoloration/removing of toxic dyes from wastewater [9].

The thesis is divided into 10 distinct chapters as follows:

- A literature study that for the first time critically reviews platinum recovery methods using porphyrinic derivatives (**Chapter 1**)
- The equipment used for the physico-chemical characterization of the materials obtained and the monitoring of the experiments in real time (**Chapter 2**).
- The following seven chapters (**Chapters 3-9**) present the experimental results and the working procedure for each individual study:
  - Obtaining basic porphyrins using the multicomponent Adler-Longo method
  - Direct metalation of porphyrin-bases
  - Physico-chemical characterization of the new porphyrinic structures obtained
  - Fluorimetric and electrochemical detection of hydrogen peroxide using Pt(II)-5,10,15,20-tetra-(4-allyloxyphenyl)porphyrin
  - Obtaining an optical sensor for the potassium salt of 1-anthraquinonesulfonic acid
  - Realization of a hydroquinone fluorimetric/optical sensor
  - Detection and recovery of platinum using porphyrinic derivatives from colloidal PtNPs solutions or from aqueous solutions of hexachloroplatinic acid
  - Synthesis of multifunctional hybrid nanomaterials incorporating porphyrins and/or platinum nanoparticles used in carbon dioxide capture and in the removal of methylene blue and basic fuchsin from wastewater
- **Chapter 10** presents the general conclusions and original aspects of this thesis

The specific objectives

- Obtaining by a multicomponent synthesis method of the following porphyrin-bases:
  - ✓ ***5,15-bis-(3-hydroxyphenyl)-10,20-bis(3-methoxyphenyl)porphyrin;***
  - ✓ ***5,10-bis-(3-hydroxyphenyl)-15,20-bis(3-methoxyphenyl)porphyrin;***
  - ✓ ***5-(3-hydroxyphenyl)-10,15,20-tris-(3-methoxyphenyl)porphyrin.***
- ***Separation, purification and complete physicochemical characterization*** of the obtained porphyrins by TLC, column chromatography, UV-Vis, FT-IR,

fluorescence spectrometry, ^{1}H-NMR, ^{13}C-NMR, AFM, SEM and HRTEM microscopy.

- ***Obtaining of Pt(II)-porphyrins by direct metalation*** and complete physico-chemical characterization ***with the purpose of making sensitive materials for the formulation of new sensors***:
  - ✓ ***Pt(II)-5,15-bis-(3-hydroxyphenyl)-10,20-bis(3-methoxyphenyl)porphyrin;***
  - ✓ ***Pt(II)-5-(3-hydroxyphenyl)-10,15,20-tris-(3-methoxyphenyl)porphyrin;***
  - ✓ ***Pt(II)-5,10,15,20-tetra-(4-allyloxyphenyl)porphyrin.***
- ***Formulation of optical sensors for the quantification of quinone derivatives*** using as sensitive material: ***Pt(II)5,15-bis-(3-hydroxyphenyl)-10,20-bis(3-methoxyphenyl)porphyrin*** and ***Pt(II)-5- (3-hydroxyphenyl)-10,15,20-tris-(3-methoxyphenyl)porphyrin.***
- Realization of ***fluorimetric*** and ***electrochemical sensors for*** the ***quantification of hydrogen peroxide*** based on ***Pt(II)-5,10,15,20-tetra-(4-allyloxyphenyl)porphyrin (PtTAOPP) useful in medical and pharmaceutical/cosmetics applications***.
- Exploiting the affinity between porphyrinic derivatives and platinum (in colloidal or ionic form) to achieve the ***efficient recovery of platinum*** from solutions, while also generating products with added value.
- ***Obtaining of silica-porphyrin hybrid materials*** with targeted characteristics (chemical stability, large specific surface areas, controlled porosity) ***for CO_2 detection/capture*** and ***adsorption/discoloration of toxic dyes*** from wastewater.

Experimental results and discussion

Experimental results are discussed in Chapters 3-9, highlighting relevant and original aspects.

Chapter 3 details the Adler-Longo multicomponent synthesis method of a series of *meso*-phenyl-substituted porphyrins that are grafted with 3-hydroxy and 3-methoxy functional groups. The reaction scheme and the resulting products are shown in Figure 2.

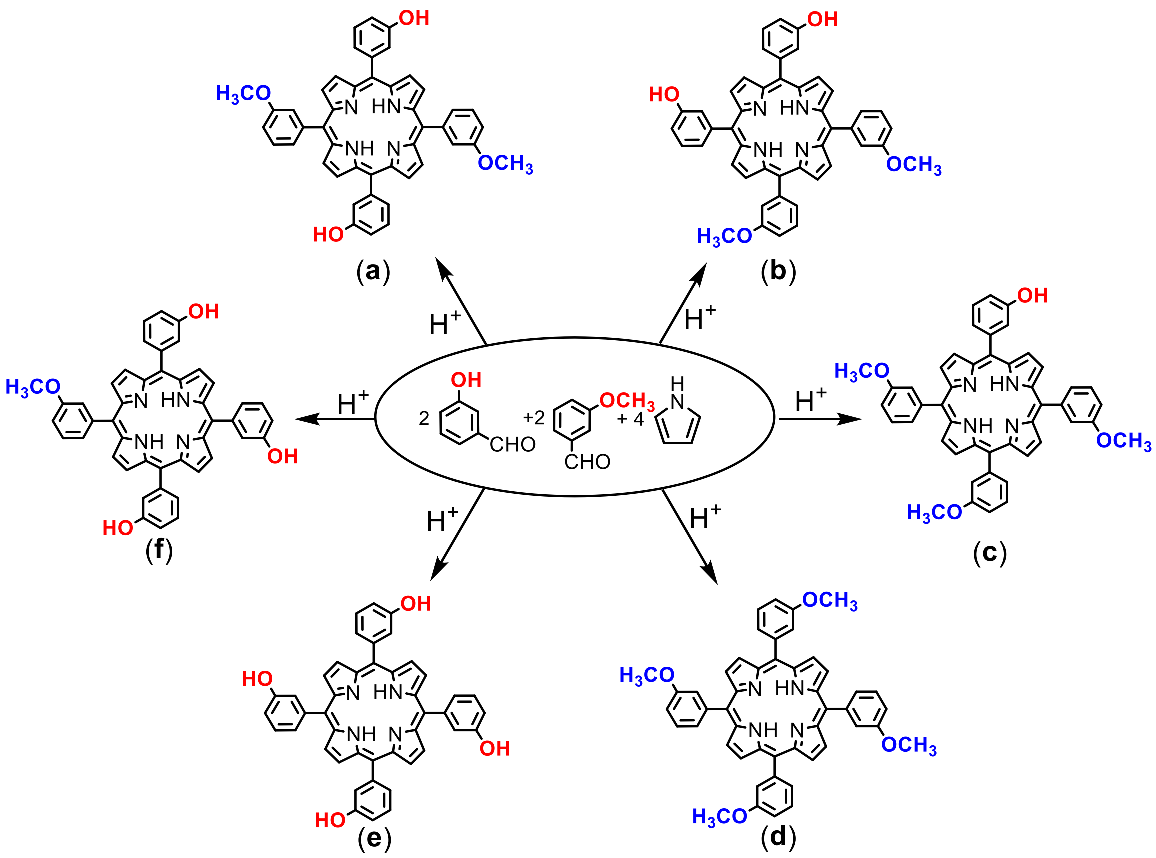

Figure 2. Chemical structure and common name of the 6 compounds resulting from the synthesis (**a**) 5,15-bis-(3-hydroxyphenyl)-10,20-bis(3-methoxyphenyl)porphyrin (**b**) 5,10-bis-(3-hydroxyphenyl)-15,20-bis(3-methoxyphenyl)porphyrin, (**c**) 5-(3-hydroxyphenyl)-10,15,20-tris-(3-methoxyphenyl)porphyrin (**d**) 5,10,15,20-tetra-(3-methoxyphenyl)porphyrin (**e**) 5,10,15,20-tetra-(3-hydroxyphenyl)-porphyrin (**f**) 5-(3-methoxyphenyl)-10,15,20-tris-(3-hydroxyphenyl)porphyrin

Among the six resulting porphyrins, the following mixed substituted structures were successfully isolated and purified in sufficient quantity:

- two tetra-substituted porphyrins of **A_2B_2** type:
  - *trans*-5,15-bis-(3-hydroxyphenyl)-10,20-bis(3-methoxyphenyl)porphyrin (Structure (**a**))
  - *cis*-5,10-bis-(3-hydroxyphenyl)-15,20-bis(3-methoxyphenyl)porphyrin (Structure (**b**))
- a tetra-substituted **A_3B-**type porphyrin:
  - 5-(3-hydroxyphenyl)-10,15,20-tris-(3-methoxyphenyl)porphyrin (Structure (**c**))

UV-Vis, ^{1}H-NMR spectra are shown below to prove the characteristic properties of the 5-(3-hydroxyphenyl)-10,15,20-tris-(3-methoxyphenyl)porphyrin structure.

The *etio* type UV-Vis spectrum of OH-3MeOPP presents the most intense Soret band at 417 nm accompanied by four Q-bands, displayed in the visible range and with increased in intensity from Q1 to QIV, as presented in Figure 3. The Soret band and the Q bands are resulted by the electron transitions from a_{1u} (π) − e_g* (π), respectively a_{2u} (π) − e_g* (π).

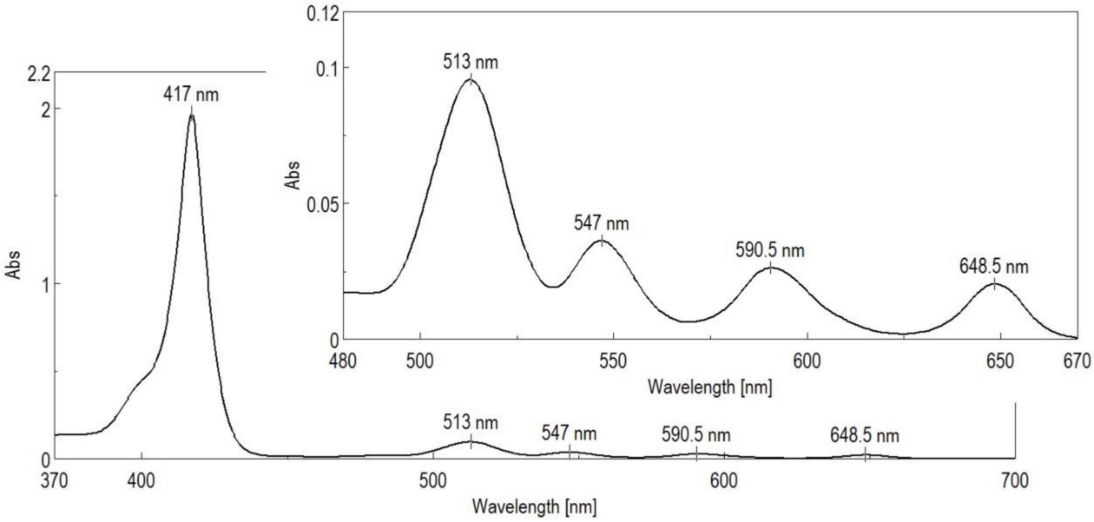

Figure 3. UV-Vis absorption spectrum of 5-(3-hydroxyphenyl)-10,15,20-tris-(3-methoxyphenyl)porphyrin

One of the proofs for obtaining of OH-3MeOPP is presented in the ^{1}H-NMR spectrum (Figure 4) that display the signal of the two shielded internal porphyrin protons at −2.79 ppm. The un-shielded β-pyrrolic protons resonate as doublet signal in the interval 8.91–8.89 ppm [10]. The aromatic protons are not completely resolved and resonate as multiplet signals in the range 8.10 – 7.33 ppm. The equivalent protons belonging to the methoxy group are assigned to the singlet at 3.99 ppm. The ratio of the integrals H_{pyrol} : $H_{(O\text{-}CH_3)}$ is approximately the calculated one of 8/9, which confirms with a good approximation the presence of three methoxy groups in the synthesized and isolated molecule.

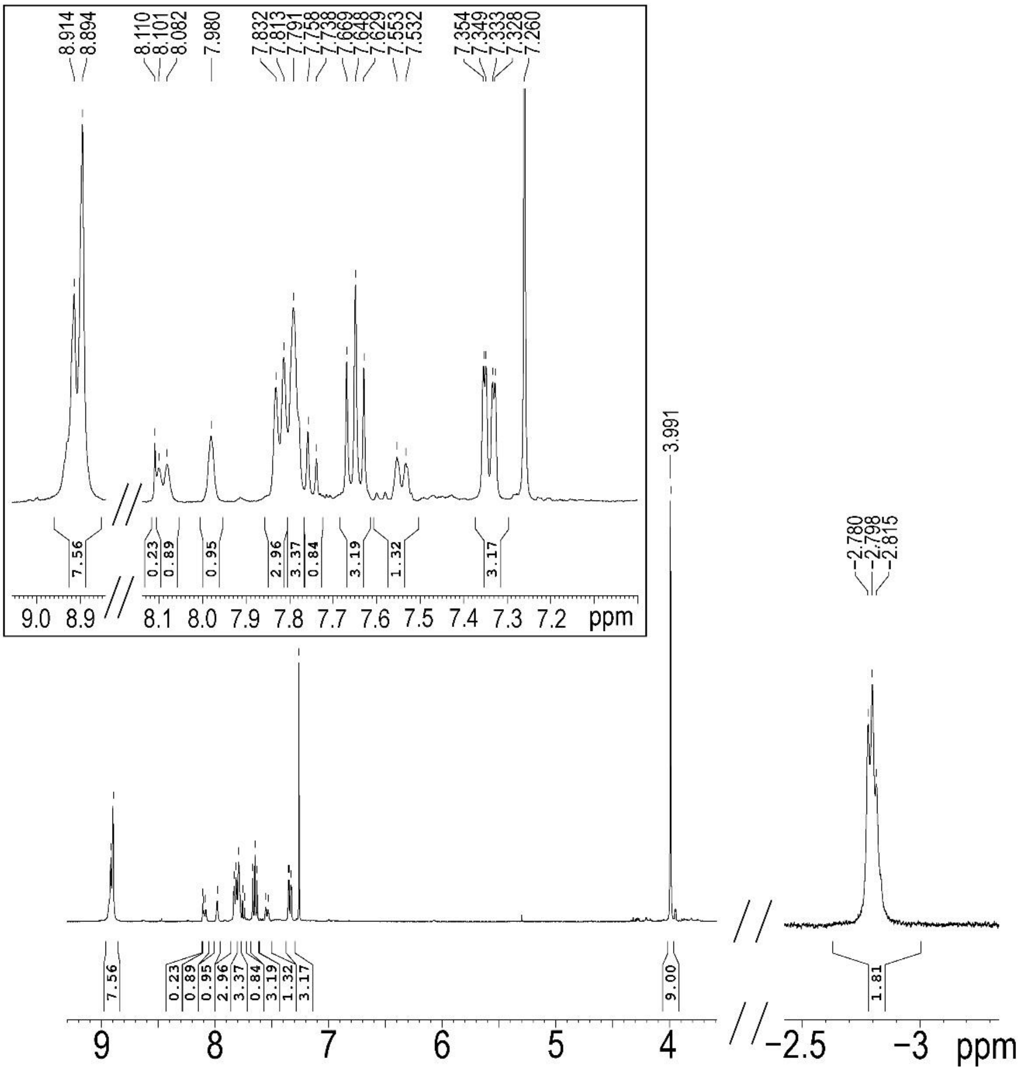

Figure 4. The ^{1}H-NMR spectrum of 5-(3-hydroxyphenyl)-10,15,20-tris-(3-methoxyphenyl)porphyrin, in $CDCl_3$, at 400 MHz

In **Chapter 4,** the synthesis and characterization of metalated porphyrinic derivatives inside the porphyrinic macrocycle with Pt(II) are presented. Metalloporphyrins were obtained by classical direct metalation of base porphyrins with a complex, namely: bis(benzonitrile)platinum dichloride.

In the framework of the thesis, three platinum - metalloporphyrins were obtained, as follows:

- Pt(II)-5-(3-hydroxyphenyl)-10,15,20-tris-(3-methoxyphenyl)porphyrins (Pt-OH-3MeOPP)
- Pt(II)-5,15-bis-(3-hydroxyphenyl)-10,20-bis(3-methoxyphenyl)porphyrin (Pt-*trans*-A_2B_2-porfirina)
- Pt(II)-5,10,15,20-tetra-(4-allyloxyphenyl)porphyrin (PtTAOPP).

These compounds were physico-chemically characterized using UV-Vis, ^{1}H-NMR, ^{13}C-NMR, AFM, SEM and HRTEM analysis methods.

The metalation reaction is exemplified for obtaining Pt(II)-5-(3-hydroxyphenyl)-10,15,20-tris-(3-methoxyphenyl)porphyrin (Pt-OH-3MeOPP) in Figure 5.

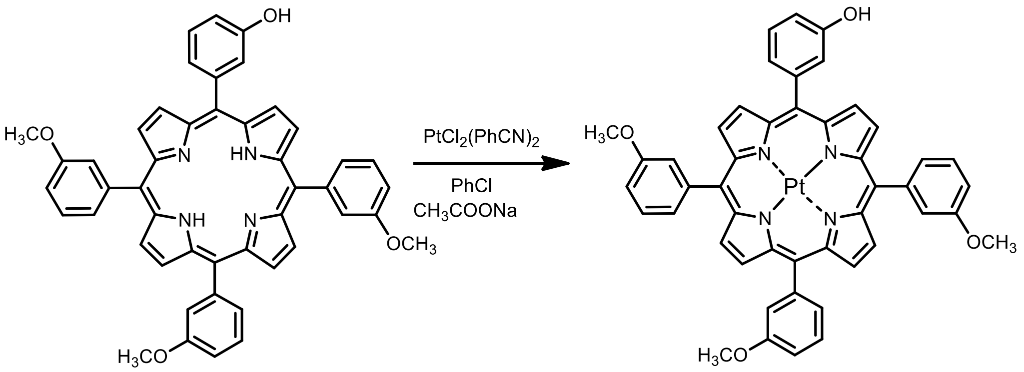

Figure 5. Reaction scheme for obtaining Pt(II)-5-(3-hydroxyphenyl)-10,15,20-tris-(3-methoxyphenyl)porphyrin

The Pt-OH-3MeOPP produces in UV-Vis spectrum a considerable blue shifting of the Soret band in comparison with the porphyrin-base, from 417 nm to 400.5 nm. From Figure 6, due to increasing in symmetry of the metalloporphyrin, a reduction of the number of Q bands from four in the porphyrin base to two in the Pt-porphyrin can be notified, accompanied by a small hypsochromic shift (5 nm).

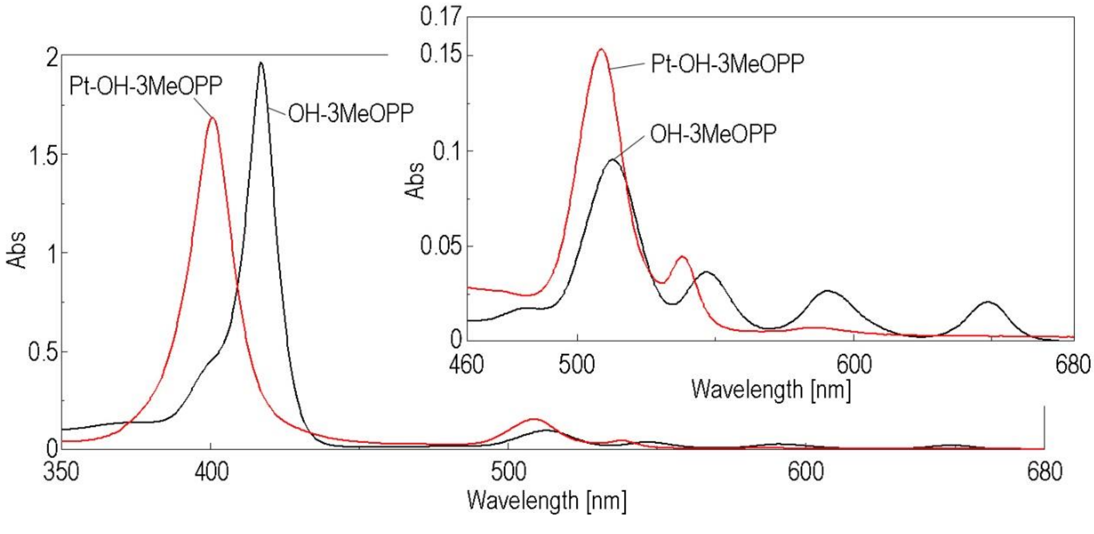

Figure 6. Comparizon of UV-Vis spectra of OH-3MeOPP (c = 8.2627 × 10^{-6} M) with Pt-OH-3MeOPP (c = 9.629 × 10^{-6} M) registered in THF

The ^{1}H-NMR spectrum of Pt-OH-3MeOPP (Figure 7) confirms the platinum coordination in the porphyrin core, proved by the disappearance of the signal located at

−2.79 ppm, which is assigned to the internal NH group protons in the porphyrin-base. The insertion of the metal leads to an upfield shift of all the signals from the spectrum.

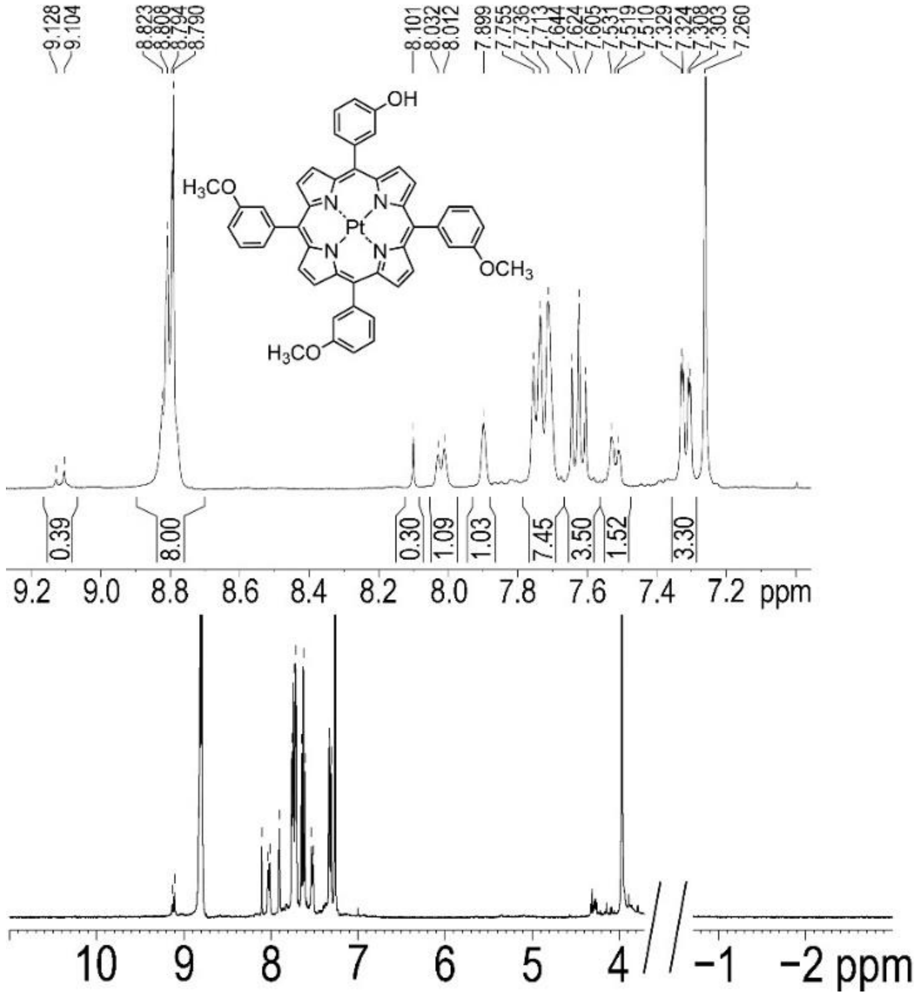

Figure 7. [1]H-NMR spectrum of the metalloporphyrin Pt(II)-5-(3-hydroxyphenyl)-10,15,20-tris-(3-methoxyphenyl)porphyrin, in $CDCl_3$, at 400 MHz

Comparing the FT-IR spectra of metalated and unmetalated porphyrin derivatives the most important issue is the absence of the internal N-H bond vibration band at about 3300 cm^{-1} in the spectrum of metalloporphyrin, that clearly demonstrated the metal coordination.

One of the synthesized metalloporphyrins, namely Pt(II)-5,10,15,20-tetra-(4-allyloxyphenyl)porphyrin was used as a sensitive substance in the detection of oxygen peroxide. The studies in **Chapter 5** cover two simple, versatile and complementary methods of H_2O_2 detection. The first presented method (fluorimetric) is based on the quenching of the fluorescence of the PtTAOPP derivative under the action of hydrogen peroxide, with a H_2O_2 detection range between 1.05 – 3.9 × 10^{-7} M. The concentration range is useful for monitoring oxygen free radicals responsible for oxidative stress.

The second detection method is based on the electrochemical behaviour of PtTAOPP in the presence of H_2O_2, useful in a range of hydrogen peroxide concentrations between $1 \times 10^{-6} - 5 \times 10^{-5}$ M, which is wider compared to that provided by the fluorimetric method. This method can be applied in the quantification of hydrogen peroxide in technical, cosmetic or agricultural fields. The multifunctionality of Pt(II)-5,10,15,20-tetra-(4-allyloxyphenyl)porphyrin by acting differently in each of the distinctively detection methods is shown schematically in Figure 8.

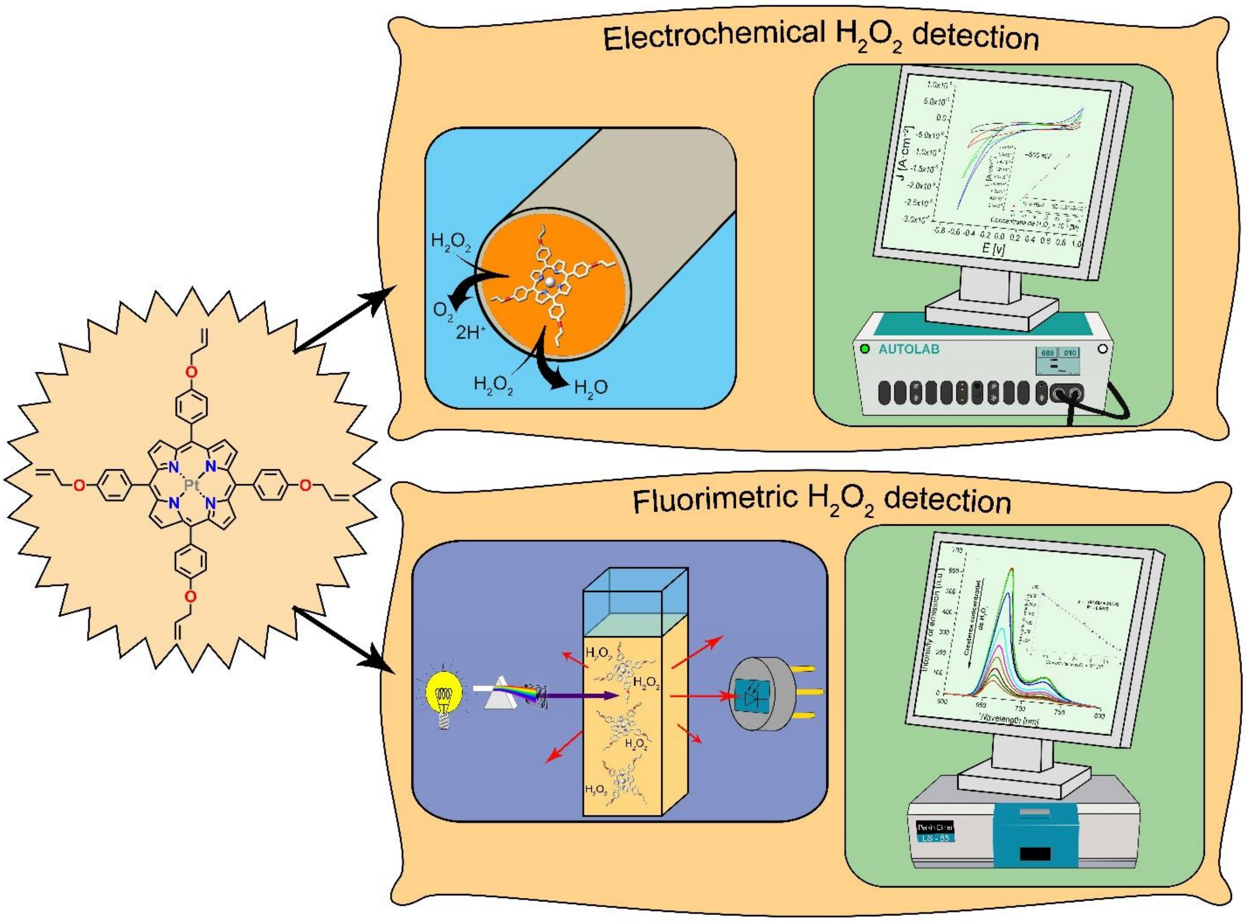

Figure 8. Multifunctionality of Pt(II)-5,10,15,20-tetra-(4-allyloxyphenyl)porphyrin as sensitive compound in the fluorimetric and electrochemical detection of hydrogen peroxide

Chapter 6 describes the creation of a new innovative optical sensor, based on the combination of gold nanoparticles (AuNPs) with Pt(II)-5,15-bis-(3-hydroxyphenyl)-10,20-bis(3-methoxyphenyl)porphyrin (Pt-*trans*-A_2B_2-porfirina), for the ***precise detection of 1-anthraquinonesulfonic acid (AQ) at very low concentrations (trace presence: 0.024 – 0.25 μM).*** The resulting hybrid material, abbreviated Pt-*trans*-A_2B_2-AuNPs (Figure 9), opens perspectives in the precise, rapid and selective monitoring of AQ (Figure 10) contained in food supplements and biological fluids

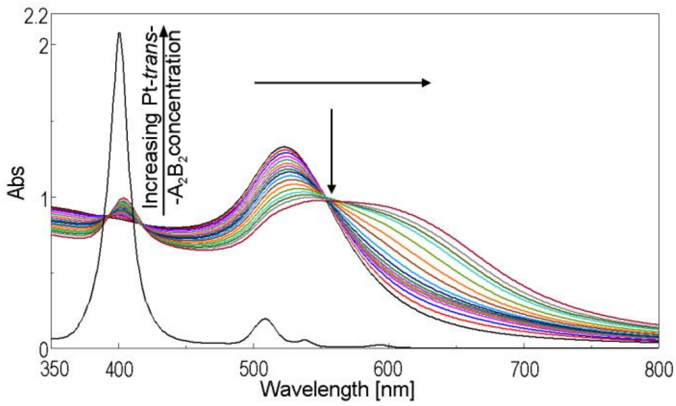

Figure 9. Obtaining of Pt-*trans*-A_2B_2-AuNPs hybrid material by introducing Pt-*trans*-A_2B_2-porphyrin to Au colloidal solution

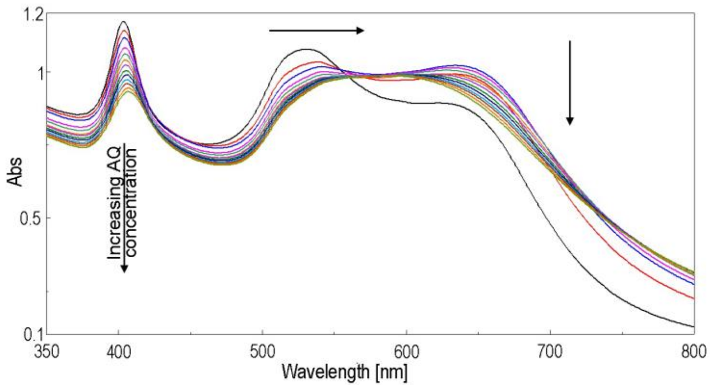

Figure 10. UV-Vis spectra when adding AQ to Pt-*trans*-A_2B_2-AuNPs hybrid material

The proposed ***AQ sensing mechanism*** (Figure 11) is based on the ***formation of hydrogen bonds*** between the peripheral –OH substituents of the porphyrin and the O=C group of AQ. The interactions between the analyte and the sensing material are potentiated by the well-known affinity of sulfur toward gold nanoparticles.

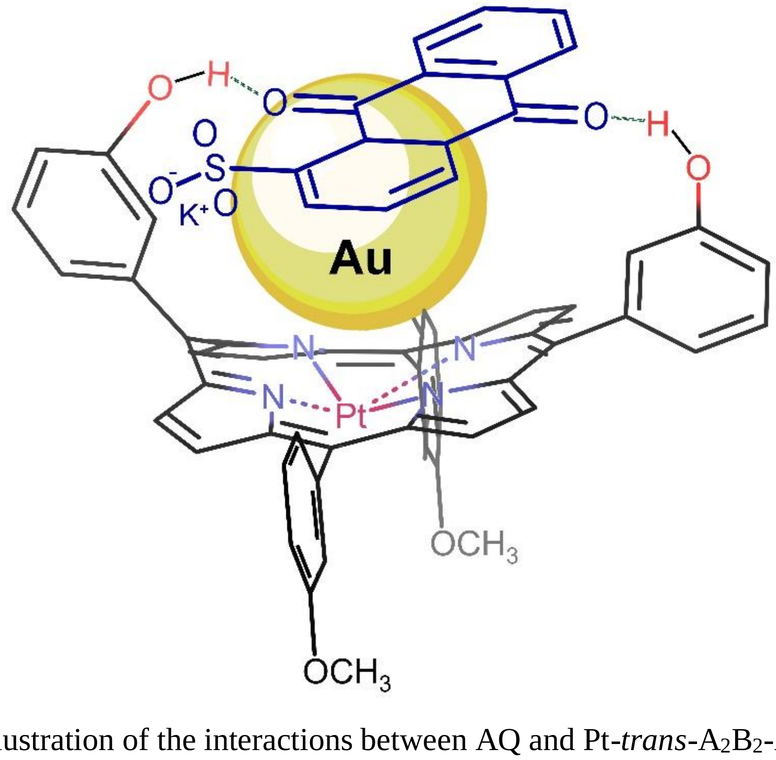

Figure 11. Illustration of the interactions between AQ and Pt-*trans*-A_2B_2-AuNPs hybrid material, justifying the sensing mechanism

Another chapter dedicated to applications, ***Chapter 7***, reported significant contributions to ***the development of new***, easy-to-use and economically feasible ***sensors for the detection of hydroquinone,*** useful for diagnosis of different pathologies (melasma, exogenous ochronosis and leukemia).

A hybrid nanomaterial, with enhanced optical properties, (Pt-OH-3MeOPP-AuNPs) was used for the optical detection of HQ. The UV-Vis monitoring of the complex formation is presented in Figure 12.

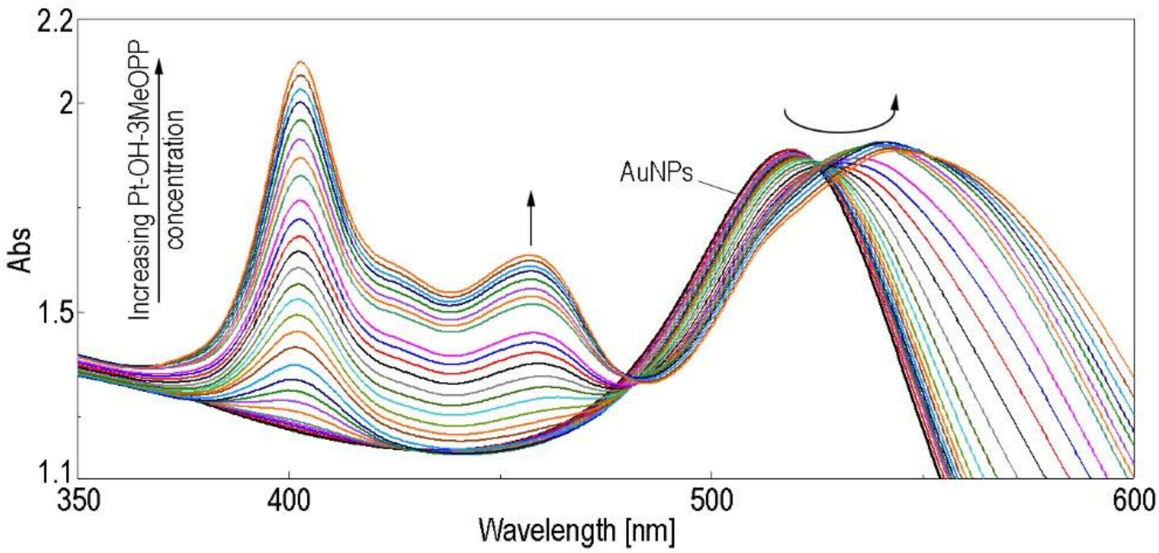

Figure 12. UV-Vis monitoring of the formation of the Pt-OH-3MeOPP-AuNPs complex in THF/water (1/9, v/v) medium

The Pt-OH-3MeOPP-AuNPs complex is a ***sensitive material for UV-Vis spectroscopic detection of hydroquinone*** in the concentration range of 3.98×10^{-8} M to 6.71×10^{-7} M. The proposed detection mechanism (Figure 13) is based on the generation of hydrogen bonds between the semiquinone form of the analyte, in acidic media, and the OH group of the porphyrin in the Pt-OH-3MeOPP-AuNPs complex

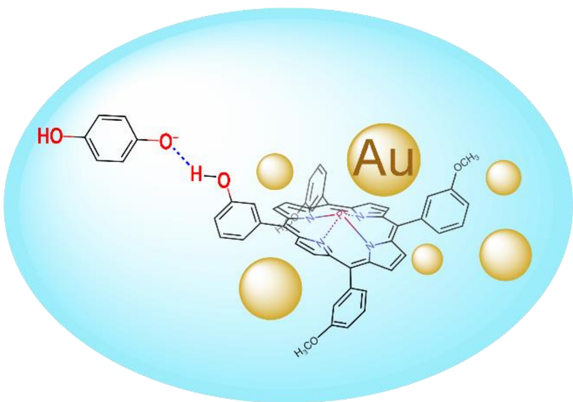

Figure 13. Detection mechanism highlighting possible interactions represented by C-O−···H type hydrogen bonds between the semiquinone and the OH group of the porphyrin

Interference tests were performed during the detection of HQ in the presence of various compounds that may be present in significant concentrations in the targeted detection media (urine and plasma). Due to significant interferences caused by iodine, ***this method cannot be used for patients with thyroid diseases, but it can be applied for all other pathologies (including diabetes)***.

The corresponding porphyrin base, 5-(3-hydroxyphenyl)-10,15,20-tris-(3-methoxyphenyl)porphyrin, which exhibits fluorescence emission, was additionally used in the formulation of a fluorimetric sensor for the quantification of hydroquinone. The sensor was sensitive in the concentration interval between 6.57×10^{-7} M and 6.35×10^{-6} M, a complementary range to that obtained with the UV-Vis spectrophotometric method. The fluorimetric method is not affected by the presence of iodine in the tested medium (***it is suitable for patients with thyroid diseases***), but it has significant errors in the presence of glucose, which does ***not allow its use in the investigation of diabetic patients***.

In **Chapter 8**, different ways of ***recovering platinum***, a noble, scarce, extremely important and difficult to replace metal in stereoselective catalytic technical applications are presented. The two methods investigated and described are: recovery of platinum ***from platinum colloidal*** solutions by complexation with porphyrins and synthesizing complexes between porphyrins grafted with different functional groups ***and hexachloroplatinic acid.*** Thus, new compounds with added value have been obtained. The structures of porphyrin-base (soluble and/or water-insoluble) and Zn(II)-metalloporphyrins that were selected for the recovery of platinum nanoparticles from colloidal solutions (PtNPs) or for their ability to complex with hexachloroplatinic acid (H_2PtCl_6) are shown schematically in Figure 14.

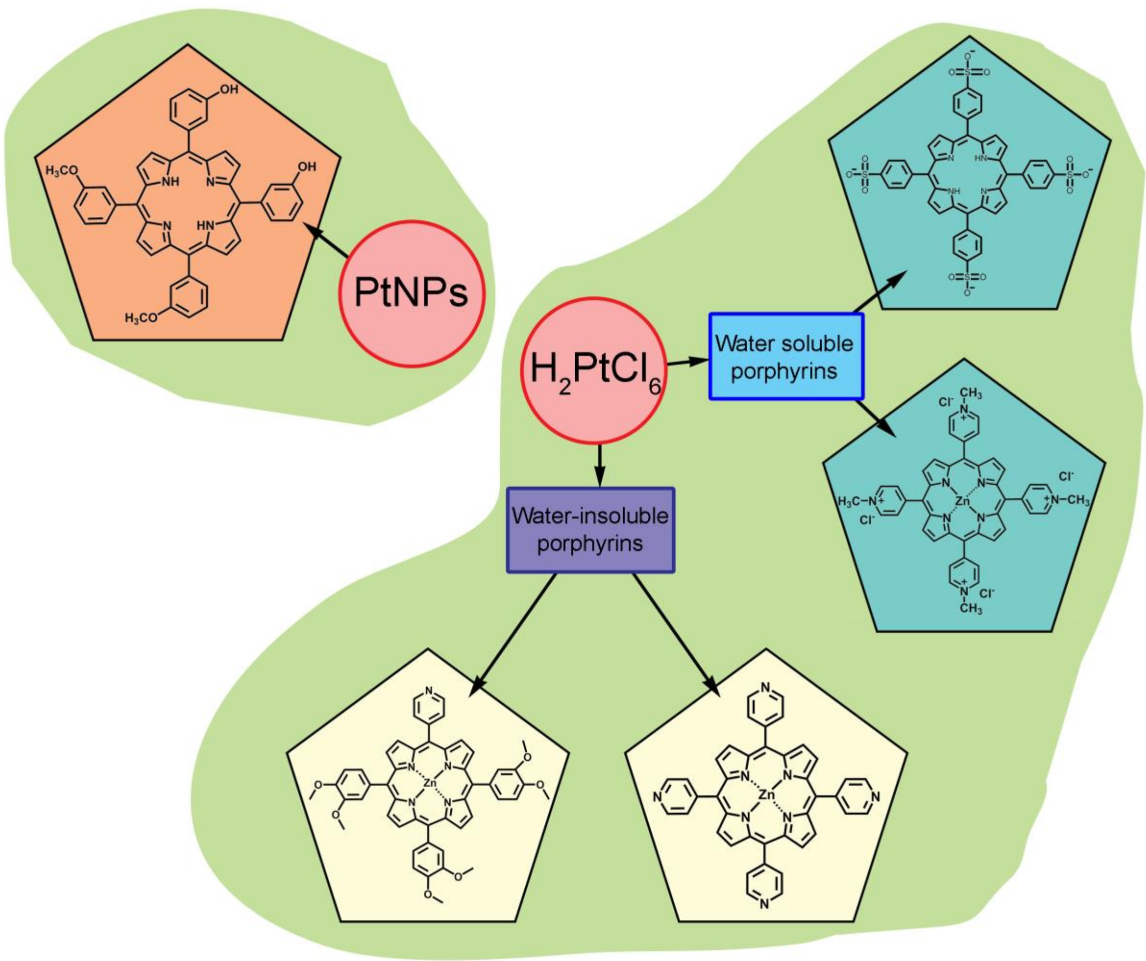

Figure 14. Porphyrin-bases, water-soluble and water-insoluble Zn(II)-metalloporphyrins used for the recovery of platinum from aqueous solutions

From the solutions resulting from hydrometallurgical processes, the compound *cis*-5,10-bis-(3-hydroxyphenyl)-15,20-bis(3-methoxyphenyl)-porphyrin is capable of detecting/recovering PtNPs with a remarkable performance of 560.904 mg of platinum / 1 g of porphyrin. Morphological studies of the surface of the complex, carried out by atomic force microscopy (AFM), showed that the porosity of the complex is significantly higher compared to that of the initial materials. The molar ratio of complexation = 1 : 2 (porphyrin : platinum) corroborated with the modification of the Q bands of the porphyrin-base, suggests that the platinum particles are not only bound in the center of the porphyrin macrocycle but also linked between the two OH groups on the periphery of the molecule, located in the position *cis*, as depicted in Figure 15.

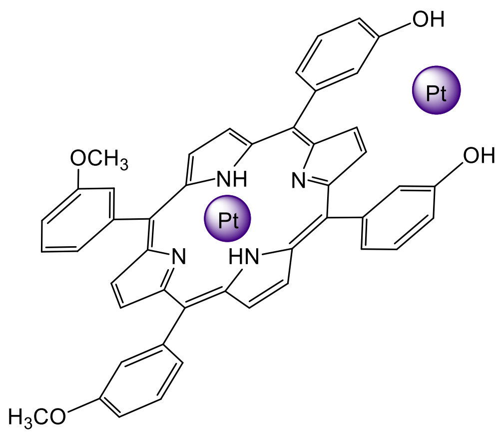

Figure 15. Representation of the complex obtained between 5,10-bis(3-hydroxyphenyl)-15,20-bis(3-methoxyphenyl)porphyrin and platinum nanoparticles. Justification of the recovery mechanism

A good detection/recovery capacity of hexachloroplatinic acid was demonstrated by the following porphyrinic derivatives: 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin (TSPP), Zn(II)-5,10,15,20-tetrakis(N-methylpyridinium-4-yl)porphyrin, Zn(II)-5,10,15,20-tetrakis(4-pyridyl)porphyrin ([ZnTMPyP]Cl_4), Zn(II)-5-(4-pyridyl)-10,15,20-tris-(3,4-dimethoxyphenyl)porphyrin (Zn-Py-3,4diMeOPP) and Zn(II)-tetrakis-pyridyl-porphyrin (ZnTPyP).

The most performing of the tested structures proved to be the tetrasubstituted 4-sulfonatophenyl porphyrin (TSPP), having a recovery capacity of 937 mg Pt/g of porphyrin, representing one of the best results reported in the specialized literature [11]. The UV-Vis spectra obtained during the addition of hexachloroplatinic acid are shown in Figure 16, where the main spectral changes are highlighted by arrows.

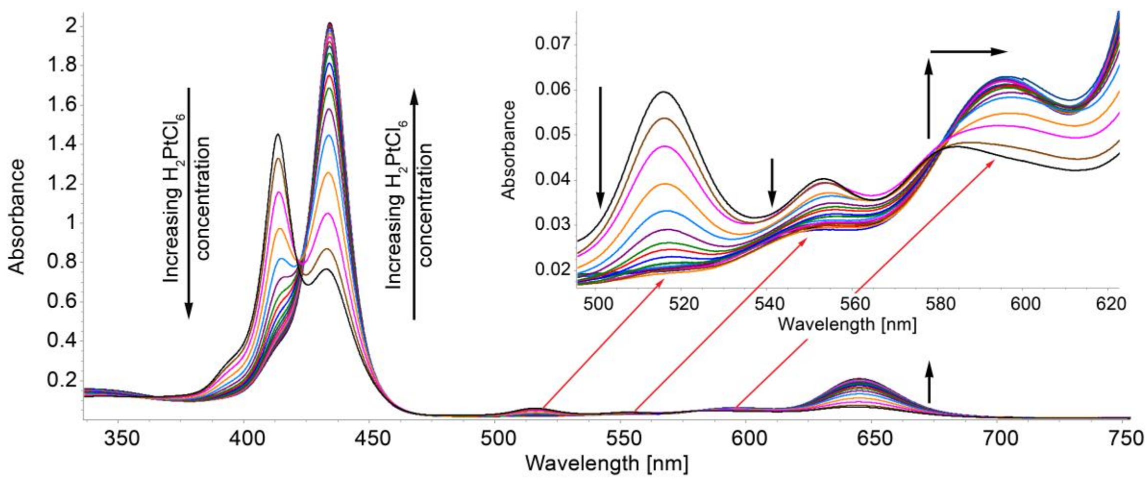

Figure 16. UV-Vis absorption spectra obtained upon the addition of hexachloroplatinic acid over the solution of 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin

Chapter 9 presents the sol-gel method for obtaining some hybrid materials by incorporating 5,10,15,20-tetra-(4-allyloxyphenyl)porphyrin (TAOPP), PtNPs or Pt(II)-5,10,15,20-tetra-(4-allyloxyphenyl)porphyrin (PtTAOPP) in silica matrices from precursor tetraethylorthosilicate (TEOS). The large specific surface areas between 600 − 740 m^2/g and large pores between 2 − 4 nm make these hybrid materials to be considered as good adsorbents. Figure 17 shows schematically the synthesis and subsequent use of these hybrid nanomaterials in the removal of methylene blue and basic fuchsia from wastewater, but also for the detection/capture of carbon dioxide.

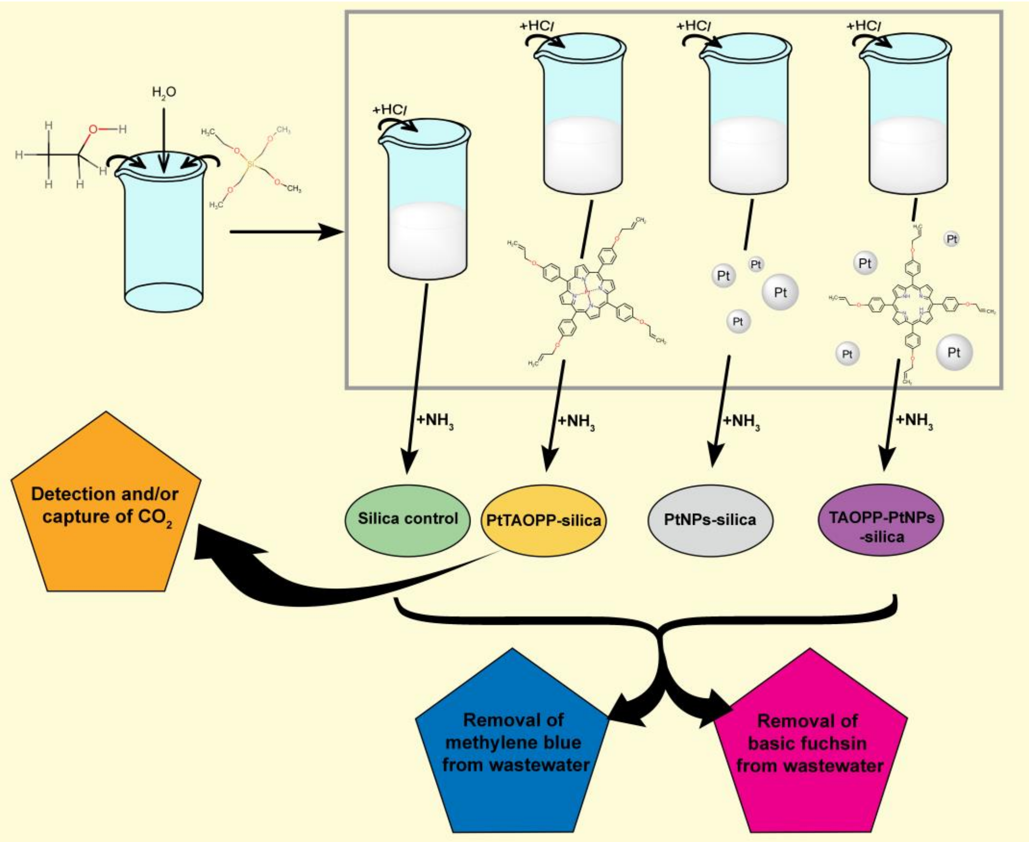

Figure 17. Graphical scheme of the method for obtaining hybrid nanomaterials based on silica matrices and their use in the removal of dyes from wastewater, respectively for the detection/capture of CO_2

The hybrid material containing the Pt-porphyrin, named ***PtTAOPP-silica***, has been used in carbon dioxide sensing and storage. Regarding gas storage, the performances are notable, as it is ***the second best result (0.025 moles CO_2/g), mentioned up to now in the literature. This achievement is considerably more valuable as it occurs under normal temperature and pressure conditions.***

The silica materials obtained and presented in this chapter have been proven to be multifunctional, being also effective ***in discoloration/removing of dyes*** from wastewaters, such as: ***methylene blue*** [8], ***basic fucsine*** [12], ***malachite green*** [13] and ***Congo red*** [14].

Adsorption tests and kinetic studies were performed for methylene blue and basic fuchsin. The best results in methylene blue tests (7.26 mg dye/g adsorbent) were obtained for the hybrid material incorporating metalloporphyrin (PtTAOPP). The same ***PtTAOPP-silica*** hybrid material is also very effective in removing basic fuchsin, a fact that are also illustrated in the photographs (Figure 18). However, the hybrid material incorporating only PtNPs in the silica matrices gave the highest basic fuchsin adsorption capacity (197.28 mg/g), probably due to the high affinity of platinum to the amine groups in the dye. Kinetic studies showed that the second-order pseudo-kinetic model fits the experimental data well, confirming that adsorption occurs involving both physical and chemical processes.

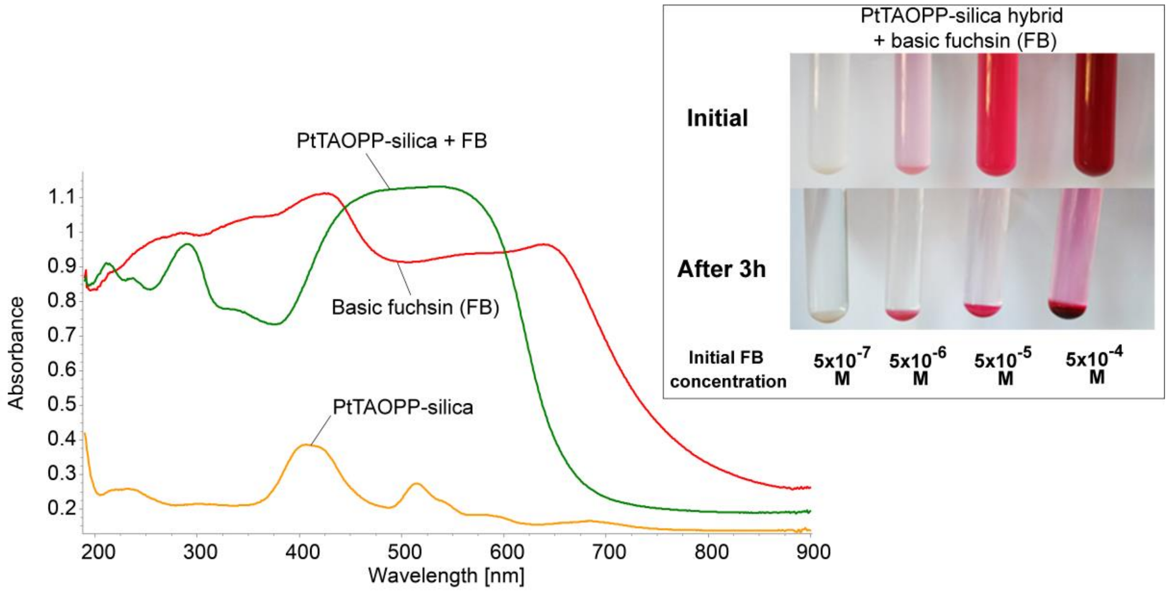

Figure 18. Comparison of the UV-Vis spectra recorded for solid ***PtTAOPP-silica*** hybrid before and after its interaction with basic fuchsin. In detail: images demonstrating the discoloration of FB solutions of different concentrations after 3-hour exposure over ***PtTAOPP-silica*** hybrid material.

Desorption studies were performed on materials that adsorbed basic fuchsin with NaOH solutions (c = 0.5 M). Figure 19 shows that the control silica can be fully regenerated. The materials thus recovered (washed with water twice and dried in an oven) can be reused at least 3 times.

Figure 19. Visual appearance of solid dye and blank silica after adsorption/desorption tests

Extract from general conclusions

The thesis has a multidisciplinary character, including knowledge from various fields: organic chemistry, physical chemistry, analytical chemistry, environmental protection and material chemistry. Corroborated studies have contributed to a comprehensive understanding of the topics addressed.

The innovative aspects of the present thesis are summarized in the diagram drawn in Figure 20.

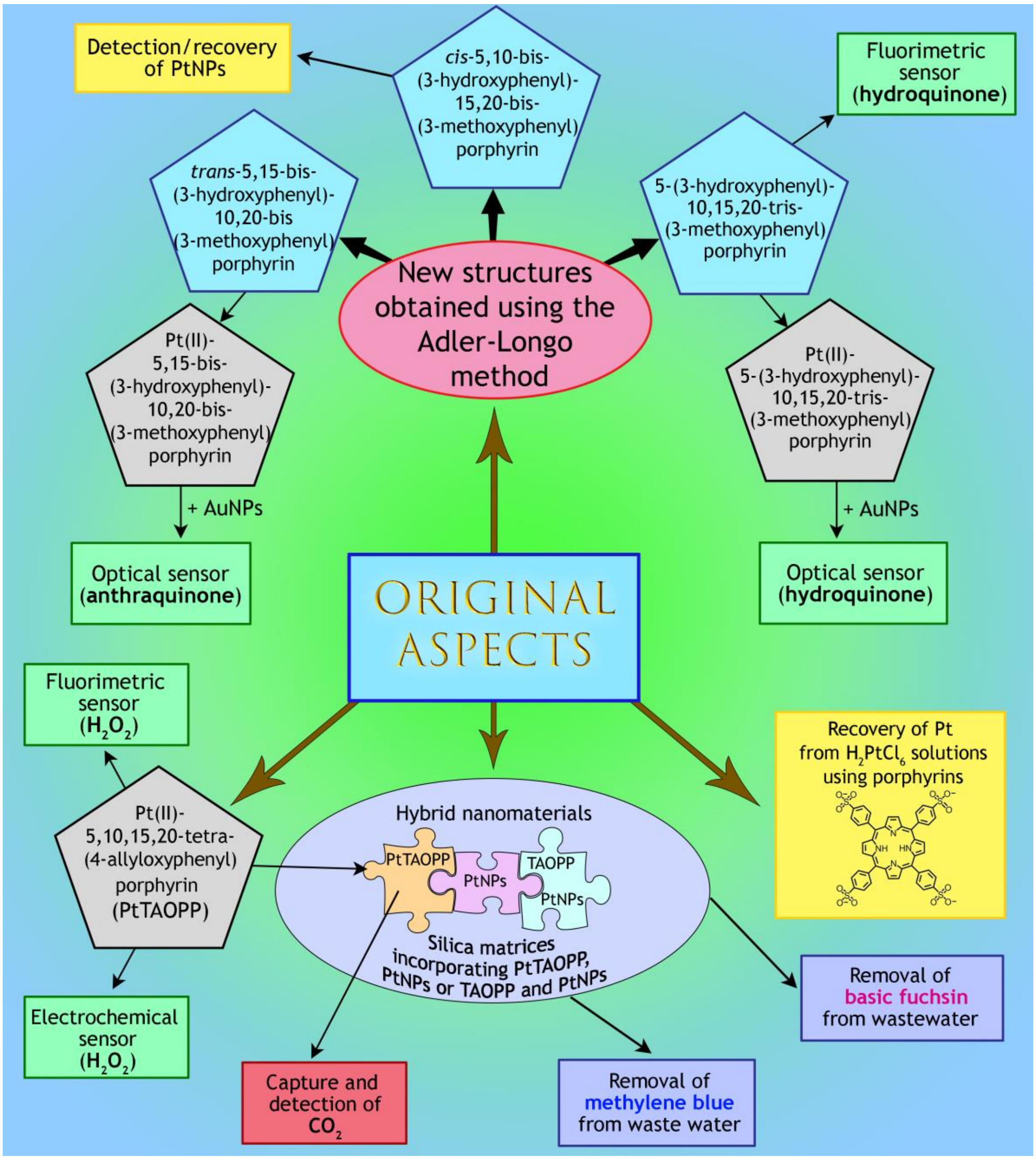

Figure 20. The main results and original aspects of this thesis, presented schematically

New results in the synthesis and characterization of compounds

❈ ***The Adler-Longo multicomponent synthesis method*** was exploited as ***an efficient way to obtain new porphyrin derivatives*** with hydroxyphenyl and methoxyphenyl substituents in the *meso* positions of the porphyrin nucleus. The synthesized new structures, separated and purified, are:

- ✓ *Trans*-5,15-bis-(3-hydroxyphenyl)-10,20-bis(3-methoxyphenyl)porphyrin (***trans*-A_2B_2-porfirina**),
- ✓ *cis*-5,15-bis-(3-hydroxyphenyl)-10,20-bis(3-methoxyphenyl)porphyrin (***cis*-A_2B_2-porfirina**)
- ✓ 5-(3-hydroxyphenyl)-10,15,20-tris-(3-methoxyphenyl)porphyrin (**OH-3MeOPP**).

❈ The following metalloporphyrins have been successfully synthesized by ***direct classical metalation***:

- ✓ Pt(II)-5,15-bis-(3-hydroxyphenyl)-10,20-bis(3-methoxyphenyl)porphyrin (**Pt-*trans*-A_2B_2-porfirina**)
- ✓ Pt(II)-5-(3-hydroxyphenyl)-10,15,20-tris-(3-methoxyphenyl)porphyrin (**Pt-OH-3MeOPP**).
- ✓ Pt(II)-5,10,15,20-tetra-(4-allyloxyphenyl)porphyrin (**PtTAOPP**).

❈ Detailed ***characterization*** to confirm the structures ***of the new compounds*** (porphyrin-bases and Pt-metalloporphyrins) was performed using several advanced analytical techniques:

- ➢ Spectrometric techniques:
  - ✓ ***^{1}H-NMR spectrometry***
  - ✓ ***^{13}C-NMR spectrometry***
  - ✓ ***FT-IR spectroscopy***
  - ✓ ***UV-Vis spectroscopy***
- ➢ Microscopic techniques:
  - ✓ Atomic Force microscopy ***(AFM)***
  - ✓ Scanning Electron Microscopy ***(SEM)***
  - ✓ High Resolution Transmission Electron Microscopy ***(HRTEM)***

The main envisaged applications of these amazing porphyrin structures are given bellow:

❈ ***Optical sensors were realized based on porphyrins for the quantification of quinone derivatives:***

- Detection and quantification of the ***potassium salt of 1-anthraquinonesulfonic acid***:
  - ✓ UV-Vis spectrophotometric method:
    - ☞ ***Pt-trans-A_2B_2-AuNPs*** which contains ***Pt(II)-5,15-bis-(3-hydroxyphenyl)-10,20-bis(3-methoxyphenyl)porphyrin***
    - ☞ concentration range between 2.419×10^{-8} M and 2.5×10^{-7} M
- Detection and quantification of ***hydroquinone***:
  - ✓ UV-Vis spectrophotometric method:
    - ☞ Pt-OH-3MeOPP-AuNPs which contains ***Pt(II)-5-(3-hydroxyphenyl)-10,15,20-tris-(3-methoxyphenyl)porphyrin***
    - ☞ the range of concentrations between 3.98×10^{-8} M and 6.71×10^{-7} M
  - ✓ fluorimetric method:
    - ☞ ***5-(3-hydroxyphenyl)-10,15,20-tris-(3-methoxyphenyl)porphyrin***
    - ☞ range of concentrations between 6.57×10^{-7} M – 6.35×10^{-6} M

❈ ***Porphyrin-based sensors for the detection and quantification of hydrogen peroxide***:

- Fluorimetric method:
  - ✓ Pt(II)-5,10,15,20-tetra-(4-allyloxyphenyl)porphyrin – sensitive material
  - ✓ H_2O_2 concentration range: 1.05×10^{-7} M – 3.9×10^{-7} M
- Electrochemical method:
  - ✓ Pt(II)-5,10,15,20-tetra-(4-allyloxyphenyl)porphyrin – sensitive material
  - ✓ H_2O_2 concentration range: 1×10^{-6} M – 5×10^{-5} M

❈ ***Pt(II)-5-(3-hydroxyphenyl)-10,15,20-tris-(3-methoxyphenyl)porphyrin exhibited remarkable multifunctionality*** because in addition to ***HQ detection ability***, this porphyrin structure has also successful applications in ***corrosion protection*** or in the ***electrocatalysis of water***. This studies are published in the *Nanomaterials* journal, that was awarded as the cover of volume 12 (number 11)/ year 2022, which contains a total of 167 articles [15].

❈ ***Porphyrinic derivatives successfully used in the recovery of platinum from solutions resulting from the recycling of spent automotive catalysts:***

- Water-insoluble porphyrins:
  - ✓ 5,10-bis(3-hydroxyphenyl)-15,20-bis(3-methoxyphenyl)porphyrin
  - ✓ Zn(II)-5,10,15,20-tetrakis(4-pyridyl)porphyrin
  - ✓ Zn(II)-5-(4-pyridyl)-10,15,20-tris(3,4-dimethoxyphenyl)porphyrin
- Water soluble porphyrins:
  - ✓ Zn(II)-5,10,15,20-tetrakis(N-methylpyridinium-4-yl)porphyrin
  - ✓ 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin (***the best recovery capacity of 937 mg Pt/g of porphyrin, one of the best results reported in the specialized literature***)

❊ ***Silica hybrid materials*** incorporating Pt(II)-5,10,15,20-tetra-(4-allyloxyphenyl)-porphyrin, PtNPs, respectively 5,10,15,20-tetra-(4-allyloxyphenyl)porphyrin with PtNPs ***proved to be multifunctional***, being also effective in ***removing the following dyes from wastewater***:

- methylene blue,
- basic fuchsin,
- malachite green,
- Congo red

❊ The ***multifunctionality of PtTAOPP*** porphyrin is notable. This metalloporphyrin can:

- function as a ***sensitive material for the detection of H_2O_2***, through two distinct methods
- successfully ***detect/store carbon dioxide*** under normal atmospheric conditions, after incorporation into a silica-based nanomaterial (PtTAOPP-silica)

Bibliography

[1] Ma, H.-C.; Sun, Y.-N.; Chen, G.-J.; Dong, Y.-B. A BINOL-Phosphoric Acid and Metalloporphyrin Derived Chiral Covalent Organic Framework for Enantioselective α-Benzylation of Aldehydes. *Chem. Sci.* **2022**, *13*, 1906–1911, doi:10.1039/d1sc06045g.

[2] Orfanos, E.; Ladomenou, K.; Angaridis, P.A.; Papadopoulos, T.; Charalambidis, G.; Vasilopoulou, M.; Coutsolelos, A.G. A Stable Platinum Porphyrin Based Photocatalyst for Hydrogen Production under Visible Light in Water. *Sustain. Energy Fuels* **2022**, *6*, 5072–5076, doi:10.1039/d2se01105k.

[3] Alemohammad, T.; Safari, N.; Rayati, S.; Gheidi, M.; Mortazavimanesh, A.; Khavasi, H. Hydrogen Bond Controlled Formation of Trans-Dihydroxo Porphyrinato Platinum(IV)

Complexes: Synthesis, Characterization and Catalytic Activity in Olefin Epoxidation. *Inorganica Chim. Acta* **2015**, 434, 198–208, doi:10.1016/j.ica.2015.05.023.

[4] Aragonès, A.C.; Martín-Rodríguez, A.; Aravena, D.; Puigmartí-Luis, J.; Amabilino, D.B.; Aliaga-Alcalde, N.; González-Campo, A.; Ruiz, E.; Díez-Pérez, I. Tuning Single-Molecule Conductance in Metalloporphyrin-Based Wires via Supramolecular Interactions. *Angew. Chem.* **2020**, *132*, 19355–19363, doi:10.1002/ange.202007237.

[5] Couto, G.K.; Pacheco, B.S.; Borba, V.M.; Junior, J.C.R.; Oliveira, T.L.; Segatto, N.V.; Seixas, F.K.; Acunha, T.V.; Iglesias, B.A.; Collares, T. Tetra-Cationic Platinum(II) Porphyrins like a Candidate Photosensitizers to Bind, Selective and Drug Delivery for Metastatic Melanoma. *J. Photochem. Photobiol. B, Biol.* **2020**, *202*, 111725, doi:10.1016/j.jphotobiol.2019.111725.

[6] Magna, G.; Muduganti, M.; Stefanelli, M.; Sivalingam, Y.; Zurlo, F.; Di Bartolomeo, E.; Catini, A.; Martinelli, E.; Paolesse, R.; Di Natale, C. Light-Activated Porphyrinoid-Capped Nanoparticles for Gas Sensing. *ACS Appl. Nano Mater.* **2020**, *4*, 414–424, doi:10.1021/acsanm.0c02754.

[7] Magna, G.; Mandoj, F.; Stefanelli, M.; Pomarico, G.; Monti, D.; Di Natale, C.; Paolesse, R.; Nardis, S. Recent Advances in Chemical Sensors Using Porphyrin-Carbon Nanostructure Hybrid Materials. *Nanomaterials* **2021**, *11*, 997, doi:10.3390/nano11040997.

[8] Anghel, D.; Lascu, A.; Epuran, C.; Fratilescu, I.; Ianasi, C.; Birdeanu, M.; Fagadar-Cosma, E. Hybrid Materials Based on Silica Matrices Impregnated with Pt-Porphyrin or PtNPs Destined for CO_2 Gas Detection or for Wastewaters Color Removal. *Int. J. Mol. Sci.* **2020**, *21*, 4262, doi:10.3390/ijms21124262.

[9] La, D.D.; Tran, C.V.; Hoang, N.T.T.; Doan Ngoc, M.D.; Nguyen, T.H.P.; Vo, H.T.; Ho, P.H.; Nguyen, T.A.; Bhosale, S.V.; Nguyen, X.C.; et al. Efficient Photocatalysis of Organic Dyes under Simulated Sunlight Irradiation by a Novel Magnetic CuFe2O4@porphyrin Nanofiber Hybrid Material Fabricated via Self-Assembly. *Fuel* **2020**, *281*, 118655, doi:10.1016/j.fuel.2020.118655.

[10] Făgădar-Cosma, E., Vlascici, D., Făgădar-Cosma, G. *Porfirinele de la sinteză la aplicații*, Eurostampa: Timișoara, România, 2008; pp 10, 13, 109

[11] Hong, H.-J.; Yu, H.; Park, M.; Jeong, H.S. Recovery of Platinum from Waste Effluent Using Polyethyleneimine-Modified Nanocelluloses: Effects of the Cellulose Source and Type. *Carbohydr. Polym.* **2019**, *210*, 167–174, doi:10.1016/j.carbpol.2019.01.079.

[12] Fratilescu, I.; Dudás, Z.; Birdeanu, M.; Epuran, C.; Anghel, D.; Fringu, I.; Lascu, A.; Len, A.; Fagadar-Cosma, E. Hybrid Silica Materials Applied for Fuchsine B Color Removal from Wastewaters. *Nanomaterials* **2021**, *11*, 863, doi:10.3390/nano11040863.

[13] RO Patent –Approved request a202000533 published in the Official Bulletin of Industrial Property (OSIM-Romania), Inventions Section, No. 2 of 20; Fratilescu, I.; Anghel, D.; Epuran, C.; Ianasi, C.; Fagadar-Cosma E. 22; Title: "Metoda de Adsorbție a Coloranților din Ape Contaminate Utilizând Materiale Hibride pe Bază de Silice Mezoporoasă care Încorporează Nanoparticule de Platină sau Pt(II)-tetra-(aliloxi-fenil)-porfirina"deposited 24.08.2020

[14] Fratilescu, I.; Fagadar-Cosma, E. Recovery of Waste Industrial Waters Containing Red Congo by Multifunctionalized Mesoporous Silica Nanomaterials. *Chem. Proc*. **2022**, *7*, 19. doi:10.3390/chemproc2022007019

[15] Fratilescu, I.; Lascu, A.; Taranu, B.O.; Epuran, C.; Birdeanu, M.; Macsim, A.-M.; Tanasa, E.; Vasile, E.; Fagadar-Cosma, E. One A_3B Porphyrin Structure—Three Successful Applications. *Nanomaterials* **2022**, *12*, 1930. doi:10.3390/nano12111930

Dissemination of results through ISI publications, peer-review journals or participation in scientific conferences or outreach events for the amateur public

The dissemination of the results carried out in the field of the doctoral thesis is presented below:

A. List of published works from the doctoral thesis material

I. Publications in international journals ISI indexed (which appear in the Web of Science database):

1) Fagadar-Cosma E.; Pleșu N.; Lascu A.; Anghel D.; Cazacu M.; Ianasi C.; Fagadar-Cosma G.; **Fratilescu I**.; Epuran C. Novel Platinum-Porphyrin as Sensing Compound for Efficient Fluorescent and Electrochemical Detection of H_2O_2 *Chemosensors.* **2020**. *8*(2), 29. https://doi.org/10.3390/chemosensors8020029; **I.F. = 5.02**

2) Anghel, D.; Lascu, A.; Epuran, C.; **Fratilescu, I**.; Ianasi, C.; Birdeanu, M.; Fagadar-Cosma, E. Hybrid Materials Based on Silica Matrices Impregnated with Pt-Porphyrin or PtNPs Destined for CO_2 Gas Detection or for Wastewaters Color Removal. *Int. J. Mol. Sci***. 2020**, *21*(12), 4262. https://doi.org/10.3390/ijms21124262; **I.F. = 5.62**

3) **Fratilescu, I**.; Dudás, Z.; Birdeanu, M.; Epuran, C.; Anghel, D.; Fringu, I.; Lascu, A.; Len, A.; Fagadar-Cosma, E. Hybrid Silica Materials Applied for Fuchsine B Color Removal from Wastewaters. *Nanomaterials.* **2021,** *11*(4), *863*. https://doi.org/10.3390/nano11040863; **I.F. = 5.719**

4) Fringu, I.; Lascu, A.; Macsim, AM.; **Fratilescu, I.;** Epuran, C.; Birdeanu, M.; Fagadar-Cosma, E. Pt(II)-A_2B_2 metalloporphyrin AuNPS hybrid material suitable for optical detection of 1-anthraquinonsulfonic acid. *Chem. Pap.* **2022**. *76*, 2513–2527. https://doi.org/10.1007/s11696-021-02047-2; **I.F. = 2.41**

5) **Fratilescu, I**.; Lascu, A.; Taranu, B.O.; Epuran, C.; Birdeanu, M.; Macsim, A.-M.; Tanasa, E.; Vasile, E.; Fagadar-Cosma, E. One A_3B Porphyrin Structure—Three Successful Applications. *Nanomaterials* **2022**, 12(11), 1930. https://doi.org/10.3390/nano12111930; ***[Editor's Choice] [Cover Issue]***; **I.F. = 5.51**

II. National patents approved and published:

1) **RO Patent–a202000533**, **Fratilescu, I**.; Anghel, D.; Epuran, C.; Ianasi, C.; Fagadar-Cosma E. 22; Titlu: "Metoda de Adsorbție a Coloranților din Ape Contaminate Utilizând Materiale Hibride pe Bază de Silice Mezoporoasă care Încorporează Nanoparticule de Platină sau Pt(II)-tetra-(aliloxi-fenil)-porfirina" **published in RO-BOPI 2/2022, from 28.02.2022**

III. Participation in international scientific events organized abroad, with poster presentation:

1) Anghel D.; Lascu A.; **Fratilescu I.**; Epuran C.; Făgădar-Cosma E., Zn-Metalloporphyrins Containing Pyridyl Groups and Their Comparative Capacity to Coordinate Hexachloroplatinic Acid, *Proceedings of the 25th International Symposium on Analytical and Environmental Problems*, Szeged, Hungary, pp 100−103, ISBN 978-963-306-702-4

IV. Participation in international scientific events, in Romania, with poster presentation:

1) **Fratilescu I.;** Epuran C.; Lascu A., Birdeanu M.; Făgădar-Cosma E. Detection of Different Quinone Derivatives Using Pt(II)-Metalloporphyrin-AuNPs Hybrid Nanomaterials. *New trends and strategies in the chemistry of advanced materials with relevance in biological systems, technique and environmental protection, 14th Edition*, October 20−21, **2022**, Timișoara, Romania, electronic volume, pp 47
2) **Fratilescu I.;** Anghel D.; Lascu A., Water soluble porphyrins used as recovery agents of platinum from leaching solutions, *New trends and strategies in the chemistry of advanced materials with relevance in biological systems,technique and environmental protection* 12th Edition, June 06−07, **2019**, Timișoara, Romania, electronic volume, pp 84
3) **Fratilescu I.;** Anghel D.; Lascu A., Făgădar-Cosma E., Water soluble porphyrin derivatives used in platinum recovery, *EmergeMAT 2nd international conference on emerging technologies in materials engineering*, November 6−8, **2019**, București, Romania

V. Participation in international scientific events, in Romania with oral presentation:

1) **Fratilescu I.** Efficient Recovery of Wastewaters Based on Beneficial Interferences Between Porphyrin Derivatives, Platinum Nanoparticles and Silica Mesoporous Matrices, *MacroYouth 2021 – ICMPP – Open Door to The Future Scientific Communications of Young Researchers 2nd Edition*, November 19, **2021**, Iași, Romania, pp 23−24
2) **Fratilescu I.;** Dudas Z.; Birdeanu M.; Epuran C.; Anghel D.; Lascu A., Făgădar-Cosma E. Hybrid Silica Materials Containing Platinum, Impregnated with Porphyrins and/or Platinum Nanoparticles for Fuchsine B Color Removal From Wastewaters. *New trends and strategies in the chemistry of advanced materials with relevance in biological systems, technique and*

environmental protection, Online Event, October 07−08, **2021**, Timișoara, Romania, electronic volume, pp 35

3) **Fratilescu, I**.; Fagadar-Cosma, E. Recovery of Waste Industrial Waters Containing Red Congo by Multifunctionalized Mesoporous Silica Nanomaterials. *17th International Symposium "Priorities of Chemistry for a Sustainable Development" PRIOCHEM.* 2022, Bucharest, Romania, October 27−29, **2021**, *7*(1), 19, https://doi.org/10.3390/chemproc2022007019

4) **Fratilescu I**.; Epuran C.; Lascu A., Birdeanu M.; Făgădar-Cosma E. Detection of Different Quinone Derivatives Using Pt(II)-Metalloporphyrin-AuNPs Hybrid Nanomaterials. New trends and strategies in the chemistry of advanced materials with relevance in biological systems, technique and environmental protection, 14th Edition, October 20−21, **2022**, Timișoara, Romania, electronic volume, pp 47

VI. Participation and dissemination actions towards the general public (pupils, students, interested persons):

1) The exhibition of an poster with the title: Water soluble porphyrins used as recovery agents of platinum from leaching solutions. Authors of the poster: **Fratilescu I**., Anghel D., Lascu A.; Event: *The 14th edition of the Night of European Researchers event*, funded by the European Commission through Marie Sklodowska-Curie actions, 27 September **2019**

B. List of works with complementary topics published as first author/co-author

I. Publications in international journals ISI indexed (which appear in the Web of Science database):

1) Birdeanu, M.; Epuran, C.; **Fratilescu, I.;** Fagadar-Cosma, E. Structured Thin Films Based on Synergistic Effects of $MnTa_2O_6$ Oxide and *bis*-Carboxy-phenyl-substituted Porphyrins, Capable to Inhibit Steel Corrosion. *Processes* **2021**, *9*(11), 1890. https://doi.org/10.3390/pr9111890; **I.F. = 3.352**

2) Epuran, C.; **Fratilescu, I.;** Anghel, D.; Birdeanu, M.; Orha, C.; Fagadar-Cosma, E. A Comparison of Uric Acid Optical Detection Using as Sensitive Materials an Amino-Substituted Porphyrin and Its Nanomaterials with CuNPs, PtNPs and Pt@CuNPs. *Processes* **2021**, *9*(11), 2072. https://doi.org/10.3390/pr9112072; ***[Feature Paper]***; **I.F. = 3.352**

3) Birdeanu, M.; **Fratilescu, I.;** Epuran, C.; Murariu, A.C.; Socol, G.; Fagadar-Cosma, E. Efficient Decrease in Corrosion of Steel in 0.1 M HCl Medium Realized by a Coating with Thin Layers of $MnTa_2O_6$ and Porphyrins Using Suitable Laser-Type Approaches. *Nanomaterials* **2022**, *12*(7), 1118. https://doi.org/10.3390/nano12071118; **I.F. = 5.3**

4) Epuran, C.; **Fratilescu, I.;** Macsim, A.-M.; Lascu, A.; Ianasi, C.; Birdeanu, M.; Fagadar-Cosma, E. Excellent Cooperation between Carboxyl-Substituted Porphyrins, k-Carrageenan and AuNPs for Extended Application in CO_2

Capture and Manganese Ion Detection. *Chemosensors* **2022**, *10*(4), 133. https://doi.org/10.3390/chemosensors10040133; ***[Cover Issue]***; **I.F. = 4.2**

5) Birdeanu, M.; Epuran, C.; **Fratilescu, I.**; Fagadar-Cosma, E. Structured composites between $MnTa_2O_6$ and porphyrins: Influence of the number of carboxylic groups grafted on porphyrins on the capacity to inhibit corrosion of steel. *Indian J. Chem. Technol.* **2022,** *29*(4), 354−366. https://doi.org/10.56042/ijct.v29i4.59344; **I.F. = 0.56**

6) Lascu, A.; Epuran, C.; **Fratilescu, I.**; Birdeanu, M.; Halip, L.; Fagadar-Cosma, E. Porphyrin Hetero-Trimer Involving a Hydrophilic and a Hydrophobic Structure with Application in the Fluorescent Detection of Toluidine Blue. *Chemosensors* **2022**, *10*(11), 481. https://doi.org/10.3390/chemosensors10110481; **I.F. = 4.2**

7) Vlascici, D.; Lascu, A.; **Fratilescu, I.**; Anghel, D.; Epuran, C.; Birdeanu, M.; Chiriac, V.; Fagadar-Cosma, E. Asymmetric Pt(II)-Porphyrin Incorporated in a PVC Ion-Selective Membrane for the Potentiometric Detection of Citrate. *Chemosensors* **2023**, *11*(2), 108. https://doi.org/10.3390/chemosensors11020108; **I.F. = 4.2**

8) Birdeanu, M.; **Fratilescu, I.**; Epuran, C.; Mocanu, L.; Ianasi, C.; Lascu, A.; Fagadar-Cosma, E. Nanomaterials Based on Collaboration with Multiple Partners: $Zn_3Nb_2O_8$ Doped with Eu^{3+} and/or Amino Substituted Porphyrin Incorporated in Silica Matrices for the Discoloration of Methyl Red. *Int. J. Mol. Sci.* **2023**, *24*, 8920. https://doi.org/10.3390/ijms24108920; **I.F. = 5.6**

9) Lascu, A.; Vlascici, D.; Birdeanu, M.; Epuran, C.; **Fratilescu, I.**; Fagadar-Cosma, E. The Influence of the Nature of the Polymer Incorporating the Same A_3B Multifunctional Porphyrin on the Optical or Electrical Capacity to Recognize Procaine. *Int. J. Mol. Sci.* **2023**, *24*(24), 17265. https://doi.org/10.3390/ijms242417265; **I.F. = 5.6**

II. Publications in non-ISI open-access international journals:

1) Anghel, D.; Lascu, A.; **Fratilescu, I**.; Epuran, C.; Plesu N.; Fagadar-Cosma E. Review about Main Requirements for Porphyrin Derivatives as Components of Dye Sensitized Solar Cells. *J. Solar Eneg. Res. Updat.* **2019** *6*, 78–86. https://doi.org/10.31875/2410-2199.2019.06.9;

III. National patents approved and published (or in the process of being published):

1) **RO Patent–a202200130,** Birdeanu, M.; Epuran, C.; **Frățilescu, I.**; Fagadar-Cosma, E. Titlu: „Procedeu de obținere de inhibitori de coroziune organizați in straturi subțiri alternative de porfirine substituite cu grupări carboxil si oxid pseudo-binar de tip $MnTa_2O_6$, realizate prin tehnica PLD", **published in RO-BOPI 9/2023, from 29.09.2023**

IV. Participation in international scientific events organized abroad, with poster presentation:

1) **Fratilescu I.;** Anghel D.; Lascu A.; Epuran C.; Făgădar-Cosma E., Platinum-Porphyrin Involved in the UV-Vis Spectrophotometric detection of Rhodamine B and Oxygen Peroxide, *Proceedings of the 25th International Symposium on*

Analytical and Environmental Problems, Szeged, Hungary, pp 133−136, ISBN 978-963-306-702-4

2) Epuran C.; Anghel D.; Lascu A.; **Fratilescu I.;** Făgădar-Cosma E., Optical Detection of Rhodamine B by Pt(II) Tetra-(4-Allyloxy-Phenyl)-Porphyrin, *Proceedings of the 25th International Symposium on Analytical and Environmental Problems*, Szeged, Hungary, pp 129−132, ISBN 978-963-306-702-4

V. Participation in international scientific events, in Romania, with poster presentation:

1) **Fratilescu I.;** Epuran C.; Anghel D.; Lascu A.; Făgădar-Cosma E. Water Advanced Antibacterial Compounds. Complexes Between 1-Methylimidazole and a Carboxy –A_3B Porphyrin, *New Trends in Chemistry Research*, 15th Edition, September, 21−22, **2023**, Timișoara, Romania, electronic volume, pp 69

2) Epuran C.; **Fratilescu I.;** Anghel D.; Lascu A. Făgădar-Cosma E. Complex Between an A_3B Porphyrin, AuNPs and k-carrageenan used for Detection of 1-Methylimidazole, *New Trends in Chemistry Research*, 15th Edition, September, 21−22, **2023**, Timișoara, Romania, electronic volume, pp 68

3) Anghel D.; Lascu A.; **Fratilescu I.;** Epuran C.; Făgădar-Cosma E. New Approaches to Biological Imaging. Coordination of Boron Compounds to Different Porphyrins for Laser Dyes and Fluorescent Labeling, *New Trends in Chemistry Research*, 15th Edition, September, 21−22, **2023**, Timișoara, Romania, electronic volume, pp 65

4) Lascu A.; Epuran C.; **Fratilescu I.;** Anghel D.; Făgădar-Cosma E. Porphyrin-based Nanomaterials Able to Quantify Water in Food Packaging *New Trends in Chemistry Research*, 15th Edition, September, 21−22, **2023**, Timișoara, Romania, electronic volume, pp 67

VI. Participation in international scientific events, abroad with oral presentation (co-author):

1) Birdeanu M.; Birdeanu A-V.; **Fratilescu I.;** Fagadar-Cosma E. Diminishing of steel corrosion in acid environment using thin bi-layer surfaces of mono-carboxyl-substituted A_3B porphyrin and $MnTa_2O_6$. Proceedings 13th International Conference on Nanomaterials - Research & Application − Nanocon 2021, October 20−22, 2021, Brno, Czech Republic, pp 448−453 ISBN: 978-80-88365-00-6. DOI: https://doi.org/10.37904/nanocon.2021.4373

2) Fagadar-Cosma E.; Birdeanu M.; **Fratilescu I**.; Birdeanu A-V.; Stamatin I. When Laser Methods Encounter Porphyrin Derivatives to Create Multifunctional Thin Layers Destined for Corrosion Inhibition and Sensor Devices. *Webinar on Laser, Optics & Photonics*, July 26−27, 2021, Greenville, USA, pp 17

VII. Participation and dissemination actions towards the general public (pupils, students, interested persons):

1) The exhibition of an poster with the title of the project PN-III-P2-2.1-PED-2019-0487, 528 PED/2020 CERAPOR-CORR, „Materiale hibride de tip ceramic / porfirine depuse ca straturi unice sau de tip sandviș prin tehnica PLD pentru inhibarea coroziuni otelurilor in mediu acid” and the graphic abstract from the paper published in Nanomaterials with the title “One A_3B Porphyrin Structure - Three Successful Applications” (https://doi.org/10.3390/nano12111930). Even: *The 18th edition of the European Researchers' Night event*, financed by the European Commission through Marie Sklodowska-Curie actions, September 30, **2022**

2) Presentation of the poster with the title: Water Advanced Antibacterial Compounds. Complexes Between 1-Methylimidazole and a Carboxy – A_3B Porphyrin; Fratilescu I.; Epuran C.; Angel D.; Lascu A.; Făgădar-Cosma E. Event: *2023 European Researchers' Night*, financed by the European Commission through Marie Sklodowska-Curie actions, September 29, **2023**.