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TRIPHENYLPHOSPHINE OXIDE DETECTION IN TRACES USING Mn(III)-5,10,15,20-TETRATOLYL-21H,23H PORPHYRIN CHLORIDE

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Considering the high toxicity of most organophosphorus derivatives for all organisms the main purpose of this work is to study the behavior of Mn(III)-5,10,15,20-tetratolyl-21H,23H porphyrin chloride (**MnTTPCl**) as sensitive species for the detection of triphenylphosphine oxide. The changes produced in UV–Vis spectra of Mn-metalloporphyrin by increasing the concentration of triphenylphosphine oxide were investigated. With increasing amount of triphenylphosphine oxide a continuous decrease in the intensity of the Soret bands was noticed. Two isosbestic points located at 483 nm and 487 nm respectively confirm the existence of two equilibria processes between the porphyrin and the phosphorus derivative. Manganese has strong affinity both to oxygen and to phosphorus atoms, so that two different types of bonds are expected, that demonstrate the ability of porphyrin to be further used as sensitive material in sensors formulation for this phosphorus compound detection. The topography of the surfaces and the geometry of the aggregates were studied by AFM microscopy for the manganese-porphyrin before and after exposure to triphenilphosphyne oxide contaminated solutions. Multilayer of triangular plate shapes of uniform sizes (380 nm) are characteristic for bare (MnTTPCl) but after its interaction with triphenylphosphine oxide the aggregates are smaller (232-247nm) and homogeneously oriented in parallel rows.

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1. Introduction

Due to the versatile chemical properties of porphyrins and their derived metalloporphyrins exhibited function of the heterocycle structure, medium and pH [1] they can be successfully used in optical applications such as sensors for the detection of various ions [2], toxic or pharmaceutical molecules [3, 4] and gases [5, 6].

Porphyrins are suitable candidates for different medical and technical applications such as photodynamic therapy photosensitizers [7-9], organic catalysts [10] and advanced optoelectronic materials [11]. Although the organometallic chemistry of normal porphyrins is intensively studied, the hyper manganese-porphyrin type is not yet sufficiently addressed. A manganese porphyrin complex was first prepared by J. Zalenski [12] and later fully investigated by J.F. Tayler [13].

Mn porphyrins have strong affinity to oxygen atoms and because the steric hindrance between the axial ligands and the porphyrin core can be minimized, they have been investigated due to their biological importance [14, 15].

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Triphenylphosphine oxide is a neurotoxic very stable polar compound excessively present in waste organic solutions from the chemical and pharmaceutical industry, being a major by-product of Wittig and Staudinger reactions or Corey-Winter procedure for converting vicinal glycols to alkenes. The acute toxicity of triphenylphosphine oxide LC50=12.2μg/mL, LC90=29.5μg/mL is higher than triphenyltin acetate so that a correct management in relationship with sustainable chemistry is strongly required [16]. This phosphorus(V) compound is known to be resistant to biological degradation so that sono-chemical degradation was applied but the result was completely unsatisfactory, because the formed by products are more toxic [17, 18].

Based on amazing axial coordination capabilities of both Mn-porphyrins and P=O ligands, this work was focused on studying the interaction between Mn(III)-5,10,15,20- tetratolyl-21H,23H porphyrin chloride (structure in Figure 1) in the presence of triphenylphosphine oxide in order to promote the detection of neurotoxic organophosphorus derivatives in traces.

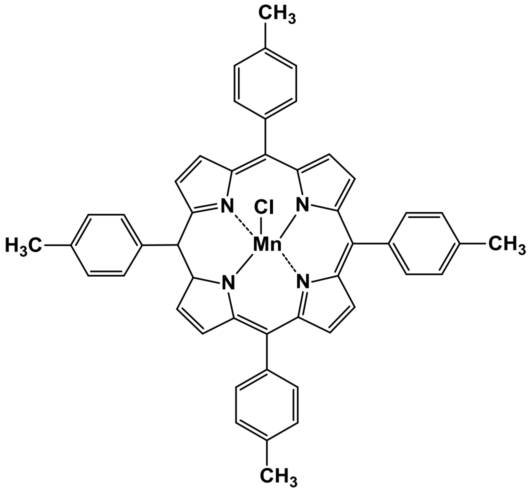

Fig. 1. Structure of Mn(III)5,10,15,20-tetratolyl-21H,23H porphyrin chloride.

2. Experimental

2.1. Reagents

All reagents used in this work were of highest purity, provided by Merck, Fluka and Sigma-Aldrich and have been used without supplementary purification. The porphyrin base, 5,10,15,20- tetratolyl-21H,23H-porphyrin, was synthesized and fully characterized according to our previous report [19]. The manganese complex was prepared by metallation of the free porphyrin [20] using large excess of manganese(III) salt (mole ratio 1/20 porphyrin/$MnCl_3$). For UV-vis measurements, 10^{-5} M stock solution of MnTTPCl and $2x10^{-4}$M solution of triphenylphosphine oxide, both dissolved in toluene, were used.

2.2. Apparatus

UV-visible spectra were recorded on a JASCO UV- V-650 visible spectrometer model (Japan) using 1 cm pass cells. Atomic force microscopy (AFM) investigations were performed on Nanosurf®EasyScan 2 Advanced Research AFM (Switzerland), equipped with a stiff (450μm × 50μm × 2μm) piezoelectric ceramic cantilever. The surface imaging was done at room temperature with samples deposited onto pure silica plates. AFM images were obtained in contact mode.

3. Results and discussion

In accordance with Figure 2, the main absorption bands of the Mn-metalloporphyrin are: two V bands (one is Soret band called V band located at 477.5 nm and Va band located at 396 nm) accompanied by two less intense Q bands (QIII band located at 621.5 nm and QIV band, located at 585 nm), and in finally so called VI band, more intense than Va band, displayed at 373 nm. In comparison with the spectrum obtained in THF, in this case the V and VI bands are bathochromically shifted, instead of Va, QIV and QIII which suffer a blue shift [21].

The UV-vis spectrum of triphenylphosphine oxide in toluene does not influence the measurements in the 300-680 nm range, because the maximum of its absorption is located at 283 nm (detail of Figure 2).

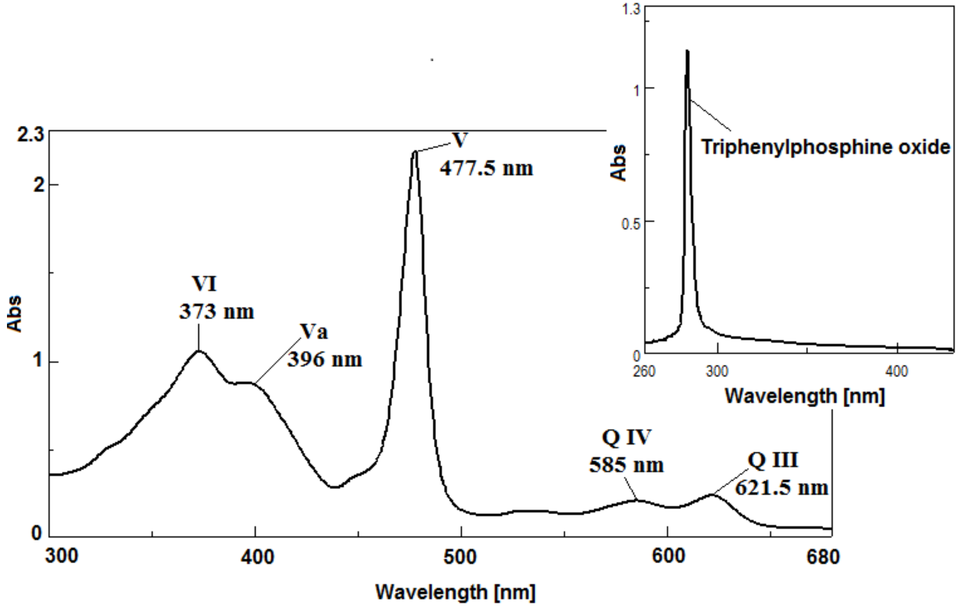

Fig. 2. Hyper type UV-vis spectrum of MnTTPCl in toluene.
In detail the spectrum of triphenylphosphine oxide

In order to detect the possible interactions between this manganese (III) porphyrin complex and triphenylphosphin oxide, a spectrophotometric titration was performed. Series of UV-Vis spectra were recorded by adding 10-100μL triphenylphosphine oxide in toluene to the basic solution consisting in MnTTPCl dissolved in toluene.

With increasing amount of triphenylphosphine oxide we noticed a continuous decrease in intensity of the Soret bands, as shown in Figure 3.

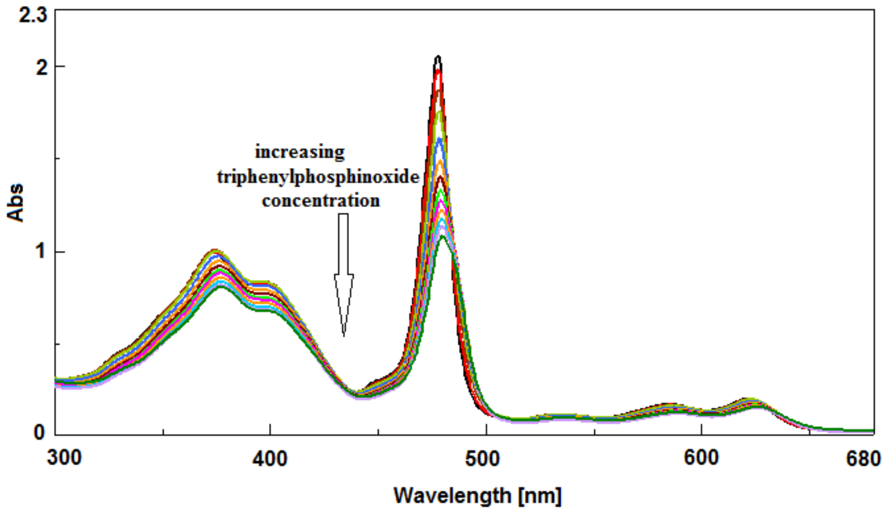

Fig. 3. Overlapped UV-vis spectra showing the effects generated by increasing concentration of triphenylphosphine oxide to MnTTPCl, in toluene.

Fig. 4 displays the efect of increasing the concentration of triphenylphosphine oxide on UV-vis spectrum of MnTTPCl for Soret band and respectively Q bands in magnified version. Two isosbestic points located at 483 nm and 487 nm respectively (Figure 4) confirm the existence of two equilibrium processes between the Mn-porphyrin and the phosphorus derivative. Based on the knowledge that manganese has strong affinity both to oxygen and to phosphorus atoms, two different types of bonds are expected to be generated during tautomeric equilibria. Besides, the oxygen center of triphenylphosphine oxide is relatively basic and due to this exhibit excellent properties to act as ligand for *hard* or *intermediate* metal centers, as manganese case is.

In the field of low concentration of triphenylphosphine oxide, the trend of the Q bands is the same as for Soret. At increased amounts, the intensity of the Q bands is increasing again, being the proof of a second process of binding.

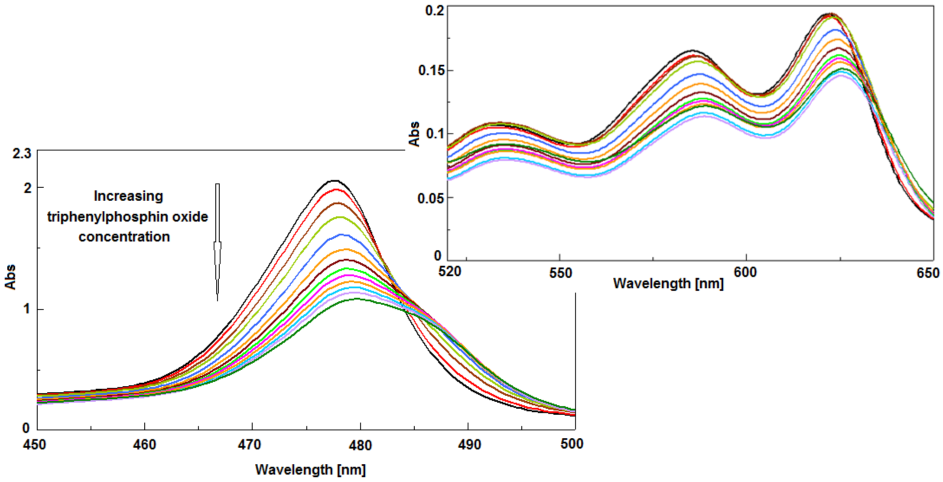

Fig. 4. The influence of increasing triphenylphosphine oxide concentration on UV-vis spectra of MnTTPCl, at Soret and Q band.

The dependence between the intensity of absorption measured at Soret band and the concentration of triphenylphosphine oxide is presented in Fig. 5 and is linear, characterized by a very good correlation coefficient of 0.984. This result demonstrates the potential of MnTTPCl to be used in optical spectroscopy analysis or as thin films based sensors after deposited by Langmuir-Blodgett or MAPLE techniques for the detection of toxic traces of triphenylphosphine oxide.

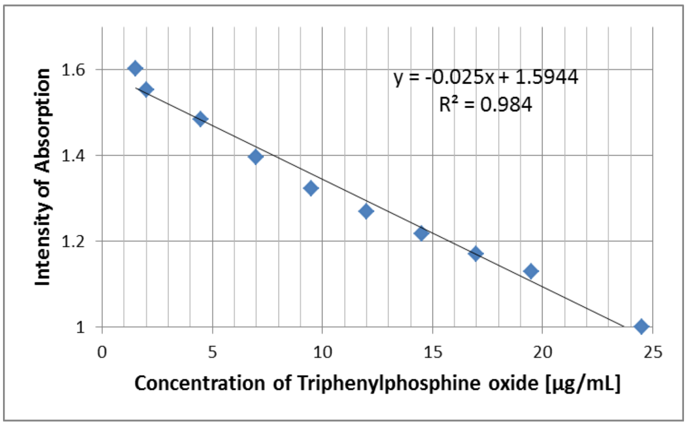

Fig. 5. The linear dependence between the intensity of absorption measured at Soret band and the concentration of triphenylphosphine oxide

Previously reported papers reveal a large potential of porphyrin to self assembly and to organize, in strictly dependence of structure and solvent in different architectures that might influence their response to different analytes [22].

The topography of the surfaces and the geometry of the aggregates was studied by AFM microscopy. The possibility of bare MnTTPCl to aggregate in toluene medium is presented in Figure 6 (different scan areas), as multilayer of platelet triangular shapes of uniform sizes (380 nm). The topography image shows large pores and the calculated roughness is around Sa = 6.4-10 nm. The peak values are distributed in the large range of 24-100 nm and the valleys depth ranges from -29 nm to - 100 nm.

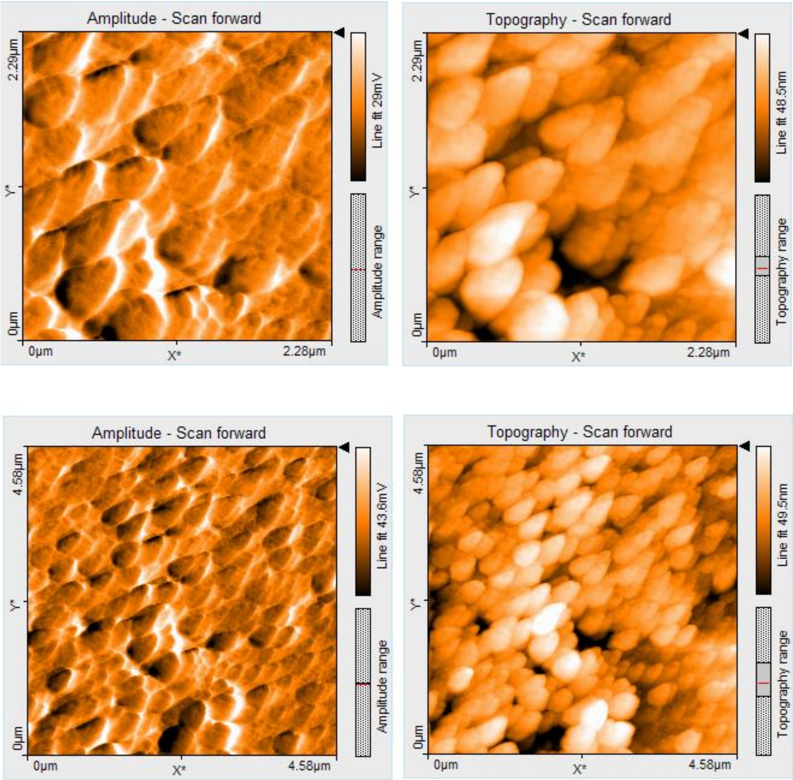

Fig. 6. AFM images at different scaned areas (2x2 µm) and (4x4 µm) of MnTTPCl from toluene, by drop casting

After introducing of triphenylphosphine oxide towards MnTTPCl, the morphology of the new surface is changed. The aggregates are smaller (232-247 nm) and similarly oriented in plane. When scanning at larger areas (9 x 9 μm) parallel rows of aggregates can be observed.

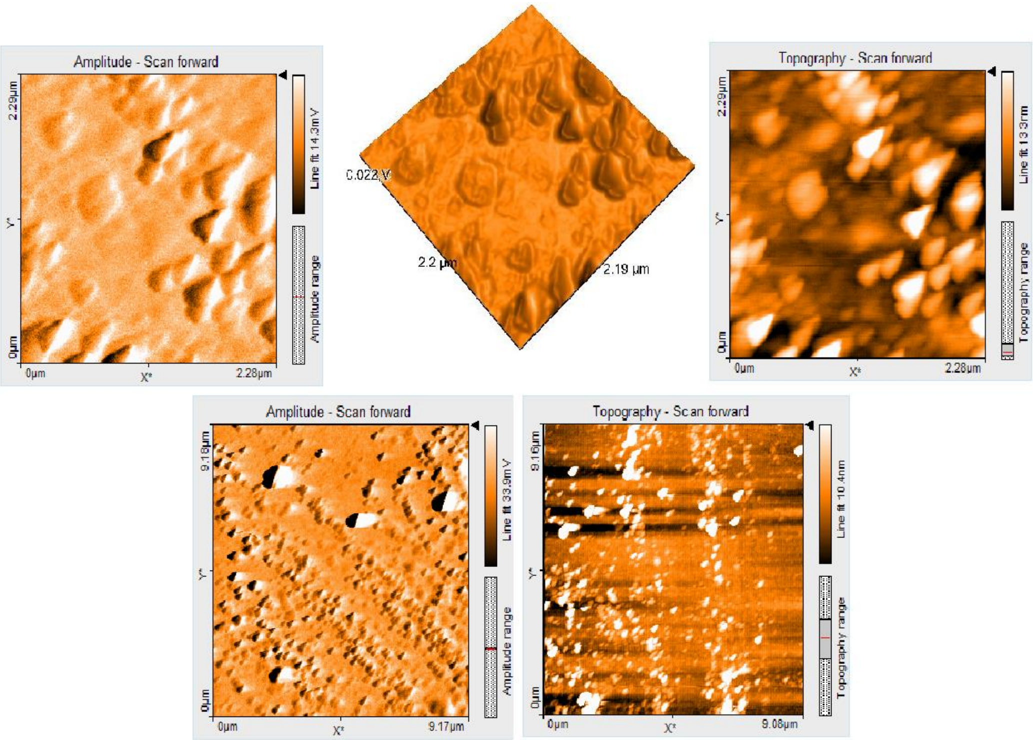

Fig. 7. 2D, 3D AFM and topography images of aggregates resulted from triphenylphosphin oxide interaction with MnTTPCl, at different scaned areas (2x2 μm) and (9x9 μm).

The roughness parameters (Sa) are decreased after exposure to triphenylphosphine oxide from 2 nm to maximum 3.3 nm and the highest peak is varying narrower (from 12 to 84 nm) in comparison with the untreated MnTTPCl surface. This changes regarding surface morphology clearly indicated that the organophosphorus compound detection is accompanied by filling of MnTTPCl pores and by novel organization of aggregates.

4. Conclusions

The porphyrins represent a fascinating world of molecules with sensational properties. Considering the high toxicity of phosphins and their derivatives for all organisms and especially for human body we try to present an UV–Vis study about the behavior of Mn(III)-5,10,15,20-tetratolyl-21H,23H porphyrin chloride in the presence of triphenylphosphin oxide.

With increasing amount of triphenylphosphine oxide we noticed a continuous decrease regarding the intensity of the Soret bands. Two isosbestic points located at 483 nm and 487 nm respectively confirm the existence of two tautomeric equilibria between the Mn-porphyrin and the phosphorus derivative. The topography of the surfaces and the geometry of the aggregates were studied by AFM microscopy and show important changes when comparing the bare MnTTPCl, which displays multilayers of triangular shapes of large uniform sizes, to the MnTTPCl after exposure to triphenylphosphine oxide, when the aggregates are smaller and reorganized in parallel rows and also the pore sizes are diminished.

Acknowledgements

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