

MANGANESE(III) PORPHYRIN SENSITIVE TO H₂O₂ DETECTION

I. CREANGA^a, A. PALADE^a, A. LASCU^a, M. BIRDEANU^{a,b},
G. FAGADAR-COSMA^c, E. FAGADAR-COSMA^{a*}

^a*Institute of Chemistry Timisoara of Romanian Academy, M. Viteazul Ave. 24,
300223-Timisoara, Romania*

^b*National Institute for Research and Development in Electrochemistry and
Condensed Matter, 1 PlautiusAndronescu Street, 300224 Timisoara, Romania*

^c*"Politehnica" University of Timisoara, 2 T. Lalescu Street, 300223-Timisoara,
Romania,*

The present study has been carried out to clarify the influence of H₂O₂ on photophysical behavior of a manganese porphyrin, namely: Mn(III)-5,10,15,20-tetra(4-methylphenyl)porphyrin chloride (**MnTTPCl**) and to reveal if this metalloporphyrin is suitable for usage as sensitive material in O₂ gas detection. Upon increasing the concentration of the H₂O₂ solution, the decrease of the absorption intensity of the Soret (V) band was noticed as a linear function with a good correlation coefficient. The capacity of the manganese porphyrin to generate aggregates was investigated by AFM in different solvents (THF and CHCl₃) before and after H₂O₂ introduction. In THF the AFM images of bare Mn-porphyrin displayed small triangular particles and platelets that are characteristic of H aggregates. These aggregates became larger but of the same shape after H₂O₂ interference. On the other side, CHCl₃ favored micro-structured ring shapes, obtained by the subsequent side by side J-process of H-types architectures, these circular geometries coexisting together with triangular or straw like structures.

(Received February 20, 2015; Accepted March 27, 2015)

Keywords: Mn-porphyrin, UV-vis spectroscopy, H₂O₂ detection, H and J aggregates, AFM

1. Introduction

Based on the knowledge that chlorophyll [1,2] is sensitive to oxygen in different concentrations, the detection of oxygen in both in the gas phase and in fluid solution using metalloporphyrins as active species attracted much attention.

One of the most important challenges is the selection of sensitive dyes that meet the high requirements of absorption, fluorescence and redox properties. Porphyrins [3], metalloporphyrins [4], their LB [5] or MAPLE thin films [6] and hybrid nanomaterials [7] are intensively used for the design of gas sensors due to their recognized active role in life processes such as: photosynthesis and oxygen transport. Manganese porphyrins, due to the manganese various oxidation states and of different values of ionic radius in 6 coordinated octahedral complexes [Mn(III) radius is 72 pm, that of Mn (II) is of 81 pm, that of Mn (IV) is 67 pm and Mn (VII) is 60 pm (100 pm=1 Å)], are interesting photocatalytic systems, able to mimetize various biological processes. Mn-porphyrins can have planar or distorted conformations and this last type might have photochemical instability, displaying amazing optical properties [8].

In the last years, oxygen-sensitive fluorophores monitoring the emission fluorescence changes, using tris(2,2'- bipyridine)ruthenium(II) or platinum(II)porphyrin dyes [9-11] were formulated.

*Corresponding author: efagadar@yahoo.com

The detection of dissolved oxygen by an optical sensor using a xerogel impregnated with palladium(II)meso-tetrakis(pentafluorophenyl)porphyrin and CdSe quantum dots has been reported [12].

Recently, the spontaneous coordination between H_2O_2 with a manganese(III)porphyrin, that led to porphyrin-Mn(V)=O species, was reported. The main purpose of this study was to design co-catalysts for selective oxidation [13].

The present study has been carried out to clarify the influence of H_2O_2 on photophysical behavior of a manganese porphyrin, namely: Mn(III)5,10,15,20-tetra(4-methyl-phenyl)porphyrin chloride (Figure 1) and to reveal if this metalloporphyrin is suitable for usage as sensitive material in O_2 gas detection.

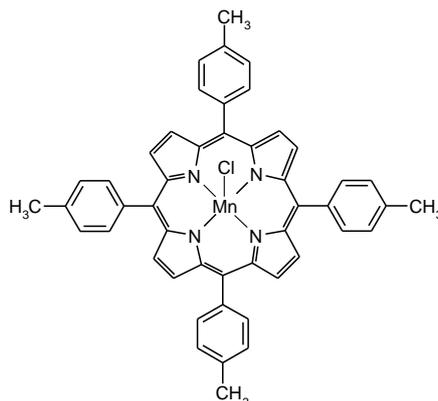


Fig. 1. Structure of Mn(III)5,10,15,20-tetra(4-methyl-phenyl)porphyrin chloride

2. Experimental

UV-visible spectra were recorded on JASCO UV-visible spectrometer, V-650 model in THF and in THF-aqueous systems, using 1 cm quartz cuvettes. AFM investigations were carried out in ambient conditions on Nanosurf[®] EasyScan 2 Advanced Research microscope and are quantitative on all three dimensions.

All reagents were provided of highest purity obtainable from Merck and Fluka and were used without further purification. All aqueous solutions were prepared with doubled distilled water. 5,10,15,20-Tetra(4-methyl-phenyl)porphyrinato manganese (III) chloride was synthesized by Adler's method [14] modified with other reported procedures [15].

3. Results and discussion

Although the Soret Band of most normal metalloporphyrins suffers a hypsochromic shift in comparison with the porphyrin free base, this situation is not produced in the case of manganese porphyrins [16].

Due to the type of donor-acceptor bonds, the absorption spectra of manganese (III) porphyrins (belonging to d-hyper type) are more complex than the UV-vis spectra of usual metalloporphyrins (belonging to normal or hypso classes) [17]. Electronic spectra of the hyper type are observed for metalloporphyrins having unoccupied orbitals in metals with symmetries $eg(d(p)-dxz)$ and dyz . The more intense band, named charge transfer band, or Soret [18] that is located around 475 nm is attributed to the transfer from the $a1u(\pi)$ and $a2u(\pi)$ orbitals of porphyrin to the manganese $eg(d(\pi))$ orbitals. Due to the disturbances produced by the e_g orbitals of manganese upon the extended π -electron system of the porphyrin ring, the QI and QII bands are shifted in the infrared region and cannot be found in the electronic spectrum.

In accordance with Figure 2, the main absorption bands of the **MnTTPCl** metalloporphyrin are: QIII band located at 624 nm; QIV band, located at 587 nm; Soret band

(called V band) red shifted at 475 nm; Va band at 397 nm and the so called VI band, more intense than Va, displayed at 371 nm.

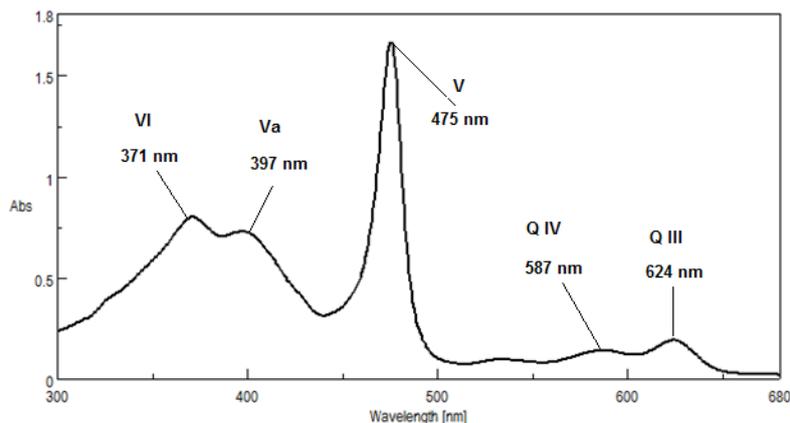


Fig. 2. Hyper type UV-vis spectrum of 5,10,15,20-tetra(4-methyl-phenyl)porphinato manganese(III) chloride

It is already known that the Mn(III) complexes might be transformed in Mn(II) porphyrins in the presence of H_2O_2 . In acidic solutions H_2O_2 acts as oxidizing agent. Under alkaline conditions Mn(II) can be oxidized by H_2O_2 to Mn(IV) species. The formation of a peroxo-bridged binuclear structure is also possible due to the fact that the hydroxide ion (formed by H_2O_2 decomposition processes) might act as an electron donor [16].

By increasing the concentration of H_2O_2 to the MnTTPCl in THF-water system, two different types of effects can be reported (Figure 3). The Soret Band together with the QIII and QIV bands are hypsochromically shifted to 470 nm, 604 and 570 nm respectively, while the Va and VI bands are bathochromically shifted to 380 and 401 nm. From the point of view of the band intensity, the Soret, QIII, Va and VI bands are characterized by an uniform decrease of intensity, instead of QIV band that suffers a continuous increase of the absorption intensity.

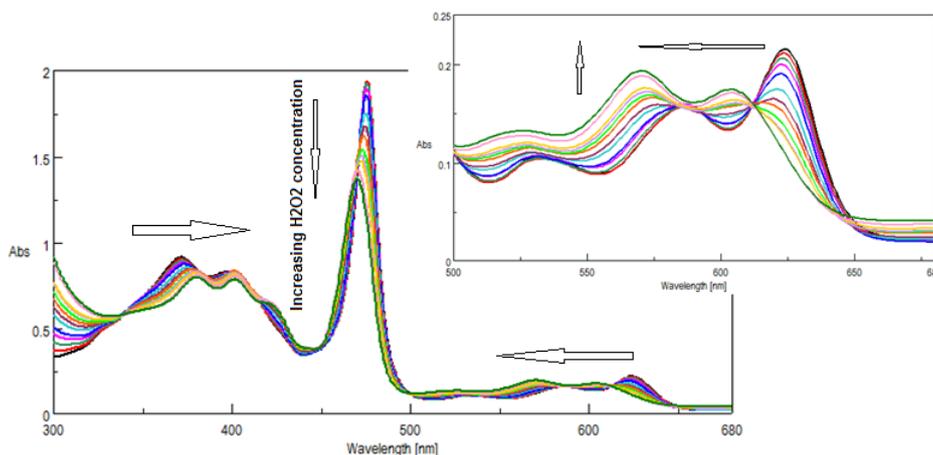


Fig. 3. Effect of increasing the concentration of H_2O_2 on UV-vis spectrum of 5,10,15,20-tetra(4-methyl-phenyl)porphinato manganese(III) chloride

This process is accompanied by the appearance of five clean isobestic points located at 340 nm, 420 nm, 450 nm, 500 nm and 620 nm. Quasi-reversible transformations of Mn(III) TTPCl \leftrightarrow Mn(II)TPP and Mn(III)TTPCl \leftrightarrow O=Mn(IV)TTP as oxo species are presumed to take place, accompanied by short-living O=Mn(V) species that might undergo one-electron reduction reactions to form again oxo-Mn(IV) species [19, 20].

Previously reports [21] explained that formation of the oxo-Mn(V) complex, accompanied by clear isobestic point at 420 nm take place in solution. Some dioxo-Mn(V) species can also be

present in solution, but the key of the whole equilibrium processes is that oxo-Mn(V) species are short-lived and are transformed into the corresponding oxo-Mn(IV) complex.

The dependence of the decrease in intensity of the Soret Band and the concentration of H_2O_2 is presented in Figure 4 as a linear function and is characterized by a very good correlation coefficient.

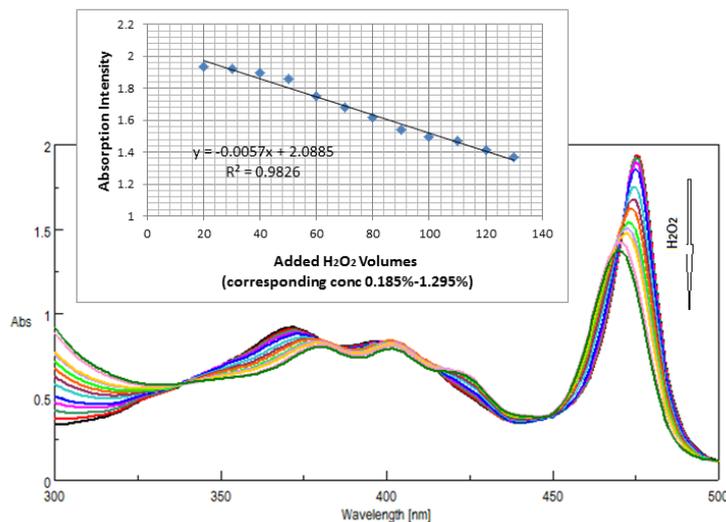


Fig. 4. The linear dependence between H_2O_2 concentration and the intensity of the Soretband in manganese(III) porphyrin UV-vis spectrum

Due to this behavior, the further attempts will be focused on the design of an O_2 sensor and in this respect the capacity of this Mn-porphyrin to develop molecular aggregates was investigated in different solvents: CHCl_3 and THF.

The topography of the surfaces and shape of the aggregates was studied by AFM microscopy. Figure 5 shows a mixture of circular geometries that co-exist with smaller triangular or straw type aggregates. The 2D and 3D contact mode AFM images clearly illustrated the ring organization (formed by J aggregation process of the initial triangular/straw H aggregates) of the manganese (III) -porphyrin at the interface air/ CHCl_3 , before the treatment with H_2O_2 . The diameter of the rings is of various sizes in the range of 200 nm and 3 μm . The mean diameter of the particles, as resulted from AFM particle analyses, was around 100 nm. The height distribution of the rings is in the range of 10-24nm.

The average surface roughness (S_a) is of 15nm, maximum peak height (S_p) has the value of 24 nm and maximum valley depth (S_v) is -7.3 nm. All were calculated based on several images for each sample.

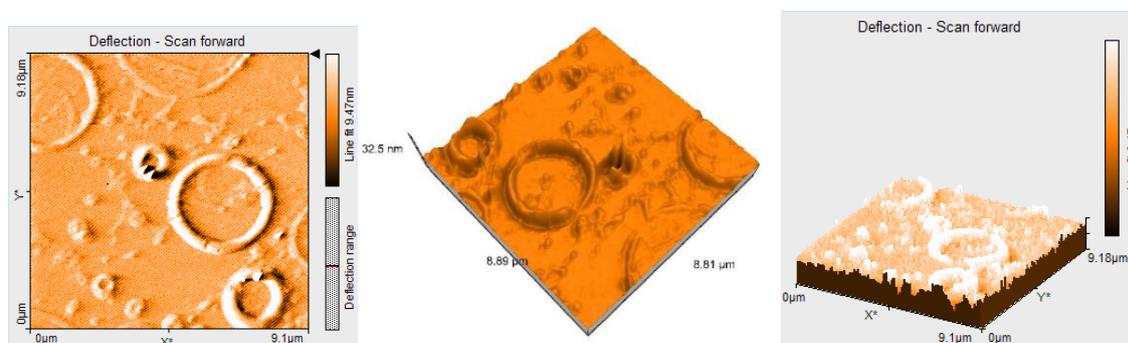


Fig. 5. 2D and 3D AFM images of baremanganese(III) porphyrin H and J-aggregates at the interface CHCl_3/air

At THF/air interface 2D and 3D AFM images of large surface areas, ($9\ \mu\text{m} \times 9\ \mu\text{m}$) (Figure 6), clearly evidenced that Mn-porphyrin forms only triangular deposits of around 380 nm, that are oriented in the same direction. A single type of aggregation face-to-face or H-type is acting.

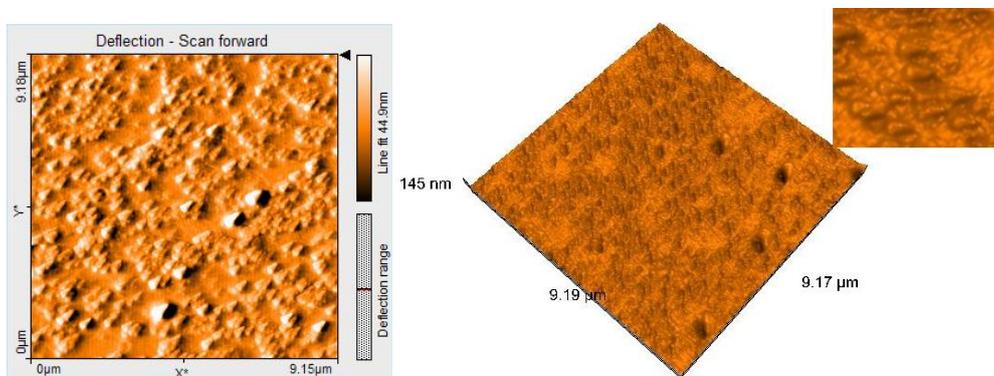


Fig. 6. 2D and 3D AFM images of bare manganese(III) porphyrin H-aggregates at the interface THF/air

After H_2O_2 treatment, the AFM measurements performed at the THF/air interface put into evidence the same architectures of aggregates existing before the H_2O_2 introduction, but of highly increased dimensions. The orientation is clearly preserved. The dimension of the large triangular geometries are from 270 nm up to 430 nm, the height distribution is in the range of 24-140 nm, the maximum peak height (S_p) has the value of 76 nm and the maximum valley depth (S_v) is -49 nm.

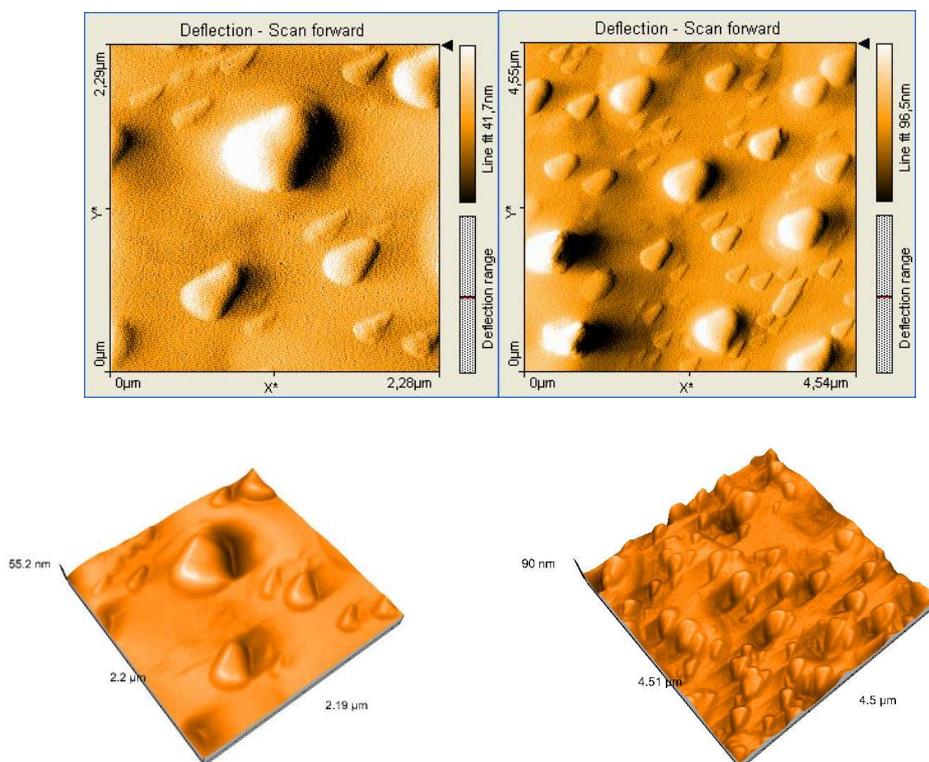


Fig. 7. 2D and 3D AFM images of manganese(III) porphyrin H-larger aggregates at the interface THF/air after H_2O_2 detection.

4. Conclusions

The present study has been carried out to clarify the influence of H₂O₂ on photophysical behavior of a manganese porphyrin, namely: Mn(III)5,10,15,20-tetra(4-methyl-phenyl)porphyrin chloride and to reveal if this metalloporphyrin is suitable for usage as sensitive material in O₂ gas detection. Upon increasing the concentration of the H₂O₂ solution, the decrease of the absorption intensity of the Soret (V) band was noticed, as a linear function with a good correlation coefficient. This decrease in intensity of absorption is accompanied by a hypsochromic shift of Soret, QIII and QIV bands. Instead, the Va and VI bands are red shifted. The five clear isosbestic points put into evidence equilibriums between various type of intermediates of Mn –porphyrin, and highly reactive forms of oxo-Mn (IV) and Oxo-Mn (V). The capacity of the manganese porphyrin to generate aggregates was investigated by AFM in different solvents (THF and CHCl₃) before and after H₂O₂ introduction. In THF, the AFM images of Mn-porphyrin displayed small triangular particles and platelets that are characteristic of H aggregates. CHCl₃ seemed to favor micro-structured ring geometries obtained by the side by side J-process, coexisting together with triangular or straw like structures.

Acknowledgements

The authors from Institute of Chemistry Timisoara of Romanian Academy are kindly acknowledging the support from Program 3-Porphyrins/2015 and STAR Programme, SAFEAIR Project 76/2013.

References

- [1] A. A. Ryan, M. O.Senge, *Photochem.Photobiol.Sci.*(2015), DOI: 10.1039/x0xx00000x;
- [2] R. C.A. Bevilaqua, I.Zanella, S. B. Fagan, *Chem. Phys. Lett.*,**496**,310 (2010).
- [3] E.Fagadar-Cosma, D.Vlascici, G.Fagadar-Cosma, A. Palade, A. Lascu, I. Creanga, M. Birdeanu, R. Cristescu,I.Cernica, *Molecules*, **19**, 21239 (2014).
- [4] M. Popescu, I. D. Simandan, F. Sava, A. Velea, E. Fagadar-Cosma, *Digest Journal of Nanomaterials and Biostructures*, **6**(3), 1253 (2011).
- [5] L.Baschir, E. Fagadar-Cosma, I. Creanga, A. Palade, A. Lascu, M. Birdeanu,;D. Savastru, V. Savu,; S. Antohe, A. Velea, G. Fagadar-Cosma, M. Popescu; I. D. Simandan, *Dig. J. Nanomater.Bios.***9**, 847 (2014).
- [6] R. Cristescu, C. Popescu, A.C. Popescu, I.N. Mihailescu, A.A.Ciucu, A. Andronie, S. Iordache, I. Stamatina, E. Fagadar-Cosma, D. B. Chrisey, *Mat. Sci. Eng. B-Adv.*, **169**, 106 (2010).
- [7] L. Lvova, M. Mastroianni, G. Pomarico, M. Santonico, G. Pennazza, C. Di Natale, R. Paolesse, A. D'Amico, *Sens. Actuators B*,**170**, 163 (2012).
- [8] O. Horvath, Z. Valicsek, G. Harrach, G. Lendvay, M. A. Fodor, *Coord. Chem. Rev.*, **256**,1531 (2012).
- [9] C.S. Chu, Y.L. Lo, *Sens. Actuators, B:Chem.* **155**,53 (2011).
- [10] Y. Zhao, T.X. Ye, H.X. Chen, D.P. Huang, T.Y. Zhou, C.Y. He, X. Chen, *Luminescence* **26**, 29 (2011).
- [11] F.H. Chu, J.J. Yang, H.W. Cai, R.H. Qu, Z.J. Fang, *Appl. Opt.* **48**, 338 (2009).
- [12] C-S.Chu, C-Y.Chuang, *Sensors and Actuators B* **209**,94 (2015).
- [13] W. Zhang, P. Jiang, Y. Wang, J. Zhang, J. Zheng, P. Zhang, *Chem. Eng. J.*,**257**,28 (2014).
- [14] A.D. Adler, F.R. Longo, F. Kampas, J. Kim, On the preparation of metalloporphyrins *J. Inorg. Nucl.Chem.* **32**,2443 (1970).
- [15] E.Fagadar-Cosma, M. C.Mirica, I. Balcu, C. Bucovicean, C.Cretu, I.Armeanu, G.Fagadar-Cosma, *Molecules*, **14**(4), 1370 (2009).
- [16] V. Valez, A. Cassina, I. Batinic-Haberle, B. Kalyanaraman, G. Ferrer-Sueta, R. Radi, *Archives Biochem.Biophys.***529**, 45 (2013).

- [17] T.N. Lomova, B.D. Berezin, Russian J. of Coord. Chem./Koordinatsionnaya Khimiya, **27** (2), 85 (2001).
- [18] L.J. Boucher, Coord. Chem. Rev. **7**, 289 (1972).
- [19] N.S. Trofimova, A.Y. Safronov, O. Ikeda, Electrochim. Acta, **50**, 4637 (2005).
- [20] C.-F. Zhang, M. Chen, D.-J. Qian, Thin Solid Films, **517** (13), 3760 (2009).
- [21] D. Lahaye, J. T. Groves, J. Inorg. Biochem., **101**, 1786 (2007).