Digest Journal of Nanomaterials and Biostructures Vol. 6, No 1, January-March 2011, p. 75-80

DEPENDENCE OF OPTICAL RESPONSE ON pH OF A WATER-SOLUBLE Zn(II)-METALLOPORPHYRIN

E. FAGADAR-COSMA*, I. CREANGA, B. MARANESCU, A. PALADE,
A. LŐRINCZI[a], G. FAGADAR-COSMA[b], M. POPESCU[a]
Institute of Chemistry Timisoara of Romanian Academy, 24 M. Viteazul Ave, 300223-Timisoara, Romania
[a]*National Institute R&D of Materials Physics, 105 bis Atomistilor Str., 077125 Bucharest-Măgurele, P. O. Box MG.7, Romania*
[b]*"Politehnica" University of Timisoara, Piata Victoriei No. 2, 300006-Timisoara, Romania*

Nowadays, porphyrin derivatives are extensively used as analytical reagents. This work put the basis for a rapid, simple and inexpensive method developed for pH determination. It was demonstrated the potential for a water soluble metalloporphyrin, 5,10,15,20-tetrakis(N-methyl-4-pyridyl)porphyrin-Zn(II) tetrachloride (**Zn-TNMPyP**) to be a potential optical pH sensor in the 5.5-10.5 domain. Monitoring of the variations in the absorption spectra of the **Zn-TNMPyP**, both regarding the Soret and the Q(0,1) band, generated by the exposure to different base concentrations allowed us to notice the linearity of the response at different pH values.

(Received Novembert 20, 2010; accepted December 14, 2010)

Keywords: Zn-metalloporphyrin, UV-vis spectroscopy, Optical pH sensor, Luminescence spectroscopy

1. Introduction

Due to their amazing optical, electrochemical and coordination properties, porphyrin derivatives (especially *β* and *meso*-substituted) are widely used for sensors design.

Receptors for anions have been formulated based on metalloporphyrins [1, 2] and by the derivatization of the porphyrin *meso*-positions with substituents bearing appropriate functional groups [3]. A new trend consists in covalent or noncovalent binding of an analyte with a porphyrinic chromophore, giving rise to a large number of optical and fluorescent sensors. In this respect, UV–vis and ^{1}H-NMR spectroscopy has been used to detect the binding of a variety of anions such as the halides, dihydrogen phosphate, hydrogen sulfate, and acetate by a β,β'-disubstituted porphyrin, as synthetic receptor.

An expanded porphyrin was also recently reported to function as a fluorescent chemodosimeter for Ag^+ ions with high sensitivity and selectivity via near-infrared luminescence above 900 nm, a region that is free from optical interference in the visible wavelength range [4]. The introduction of a metal in the core of the free porphyrin put the basis for formulation of ditopic and tritopic receptors because of both their fluorophore and coordination properties and of their capacity to match the shape of some anions providing a proper size cavity within which binding or entrapping might take place. In particular, the molecular self-assemblies of zinc meso-tetra(4-pyridyl)porphyrin (ZnTPyP) in the presence of a surfactant was reported to give hexagonal nanoprism with a large cavity of about 19 Å [5]. Zn-porphyrins attracted researchers due to their

---

*Corresponding author: efagadar@yahoo.com

applications in obtaining advanced materials [6], HPLC stationary phase for amino acids, peptides, and oligopeptides separations [7], recycling catalysts in the epoxidation reactions of alkenes [8]. A zinc metalloporphyrin [9], was investigated for Cu^{2+} ion detection and exhibits fluorescence quenching upon binding of Cu^{2+} ion and its fluorescence can be regenerated by addition of EDTA disodium solution. So, a new fluorescent sensor for Cu^{2+} ion with high sensitivity and selectivity was achieved via two functional moieties: zinc porphyrin behaves as a fluorophore having remarkable photophysical properties, and the dipyridylamine group linked in the *meso*-position of the porphyrin provides the binding platform for copper ions. Because of great demand for monitoring of Pb^{2+}, due to its toxicity, a new optical sensor in this case based on free porphyrin was also developed [10]. Optochemical sensors based on metalloporphyrins were used in addition for the detection of alcohol vapors [11].

Based on previous work that porphyrins, metalloporphyrins and functionalized porphyrin-polymers show significant solvatochromic effects and change their optical absorption, emission and electrical conduction in strictly dependence with the environment [12-14], this work represents a rapid, simple and inexpensive method developed for pH determination. It was demonstrated the potential for a water soluble porphyrin, 5,10,15,20-tetrakis(N-methyl-4-pyridyl)porphyrin-Zn(II) tetrachloride to be a novel pH optical sensor in the 5.5-10.5 domain (the structure of **Zn-TNMPyP** is given in Figure 1). The monitoring of the variations in the absorption spectra of the Zn(II)-*meso*-(tetra-4-methylpyridinium)porphyrin tetrachloride, **Zn-TNMPyP**, both regarding the Soret and the Q band, induced by the exposure to different concentrations of NaOH allowed us to notice the linearity of the response at different pH values.

2. Experimental

Chemicals. m*eso*-Tetrakis(N-methyl-4-pyridyl)porphine**,** a water soluble porphyrin, was synthesized according to literature data [15-17], by refluxing the *meso*-tetra(pyridyl)porphyrin with an excess of methyl tosylate in *N*,*N*-dimethylformanide (DMF) for 8 hours. The tosylate counter-ion was ion-exchanged by Cl^- for improving its solubility in water. Further classical metallation in water/DMF gives **Zn-TNMPyP** [18, 19]. Acetonitrile, isopropanol, *p.a.* grade and hydrochloric acid (HCl, 36%), were purchased from Fluka and Merck and used as received.

Apparatus. UV-visible spectra were recorded on a UV/VIS PERKIN ELMER, LAMBDA 12 spectrometer and on a JASCO UV-visible spectrometer, V-650 model. The photoemission and photoexcitation spectra were recorded in distilled water, with the help of a Perkin Elmer LS55 luminescence spectrometer.

Spectroscopic studies. Absorption and fluorescence spectra were recorded at ambient temperature using 1 cm path length cells. The luminescence spectra were recorded at a 100 nm/min, with constant slit widths, for excitation (2.5 nm) and for emission (4 nm). A 515 nm cut-off filter to eliminate harmonic or scattering peaks was used. For introducing basic and acidic conditions, stock aqueous solutions of 0.1 M NaOH and 0.1 M HCl were used. The concentration of Zn-porphyrin was kept constant in all measurements. The pH values of the solutions were measured with a digital Radelkis pH-meter. The values were verified with stock Sorenson's Buffers for pH=8, pH=9 and pH=10 (provided from Feinchemie K. H. Kallies KG).

3. Results and discussion

The UV-vis spectra of 5,10,15,20-tetrakis(N-methyl-4-pyridyl)porphyrin-Zn(II) tetrachloride display the typical Soret band around 437 nm, which arose from transition of $a_{1u}(\pi)$-$e_g^*(\pi)$ and the two Q-bands with absorption maxima around 564 and 606 nm, corresponding to $a_{2u}(\pi)$- $e_g^*(\pi)$ transitions (Figure 1). The electronic-vibrational Q(0,1) band at 564 nm is more increased in intensity than Q(0,0) band located at 606 nm.

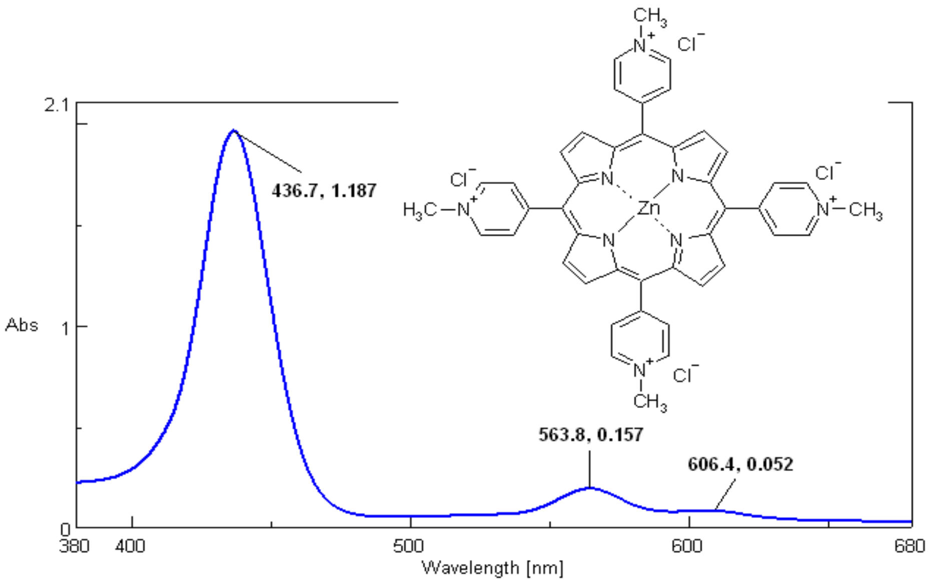

Fig. 1. UV-vis spectrum of ***Zn-TNMPyP****, in distilled water,* $C=1.215\times10^{-5}$ *mol/l (pH=5.5)*
UV-Vis (H_2O)*-λmax (logε): 436.7(5.20); 563.8(4.19); 606.4 (3.82).*

The excitation and emission spectra of **Zn-TNMPyP** were performed in isopropanol, water and acetonitrile, and the solvent dependency on the position and the intensity of the emission band is to be underlined. Although the emission spectra have similar shape, with an important band around 630-640 nm, and a shoulder at higher wavelength (670-690 nm, corresponding to porphyrin macrocycle), the position and the intensity of the bands is dependent on the polarity of the solvent. So, water induced a significant increase of the intensity and acetonitrile, which is more polar then isopropanol, produces an important bathochromic shift of the main band.

The monitoring of the variations in the intensity of the absorption spectra of the Zn (II)-*meso*-(tetra-4-methylpyridinium) porphyrin tetrachloride, **Zn-TNMPyP**, both regarding the Soret and the Q band, induced by the exposure to different concentrations of acid and base allowed us to notice the linearity of the response at different pH values in the basic domain.

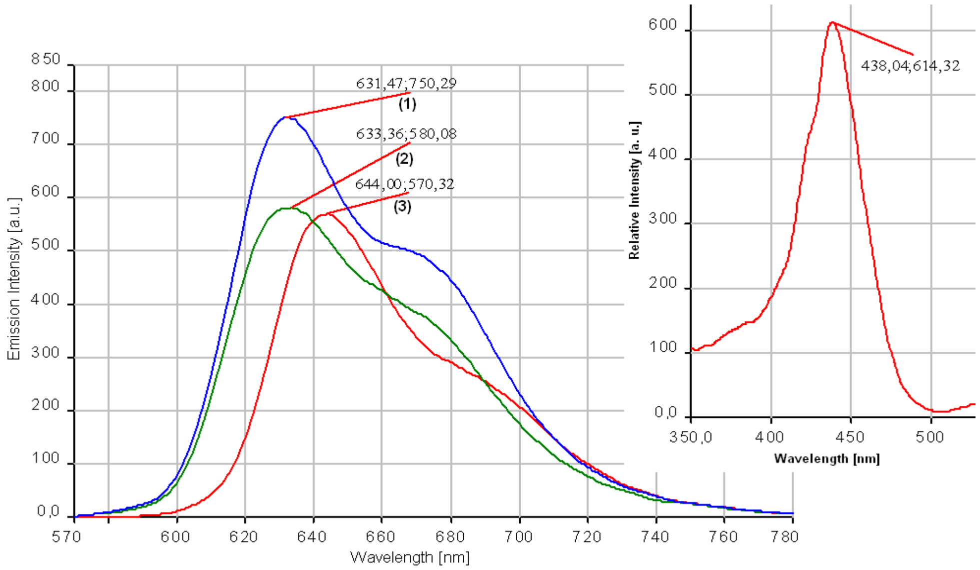

Fig. 2. Emission spectra (λex=436 nm) of ***Zn-TNMPyP*** *(constant concentration)*
in different solvents: line (1)–water, line (2)-isopropanol, line (3)-acetonitrile;
In detail - excitation spectra in isopropanol $\lambda_{em}=632$ *nm*

In acidic media (Figure 3) the intensity of the Soret and the Q (0,1) band is increasing and decreasing without obeying no rule.

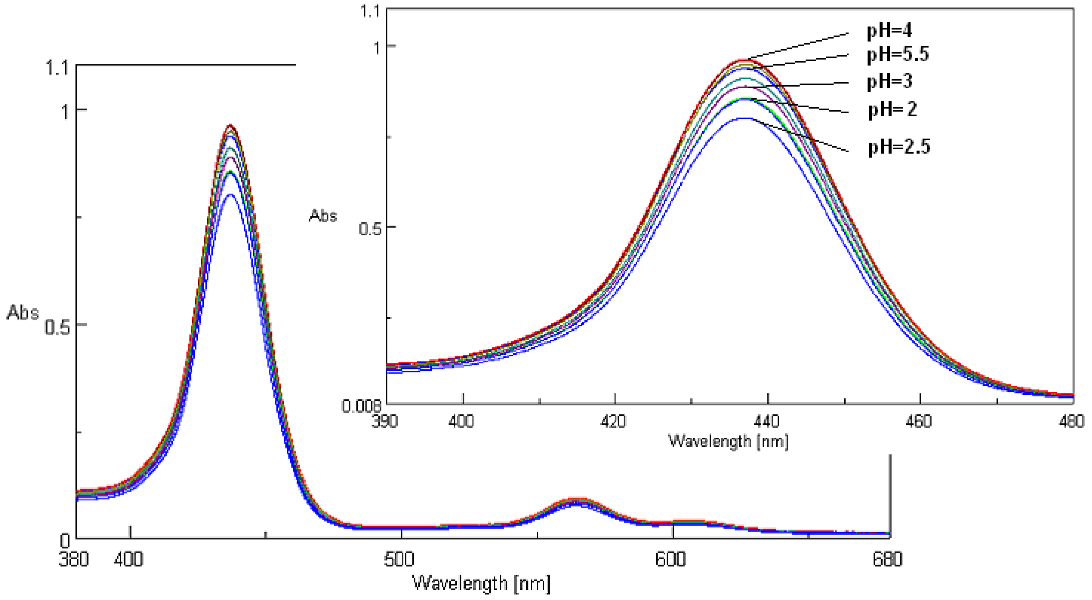

Fig. 3. The influence of acidity (pH=1.5-5.5) on Soret band of ***Zn-TNMPyP.***

Adding of base to the water solution, is producing a constant decrease of the intensity of the Soret bands and of the Q (0,1) bands, respectively, depending on the increasing of the pH of the environment, as represented below, in Figures 4 and 5. The dependence is linear in both cases with a good correlation coefficient.

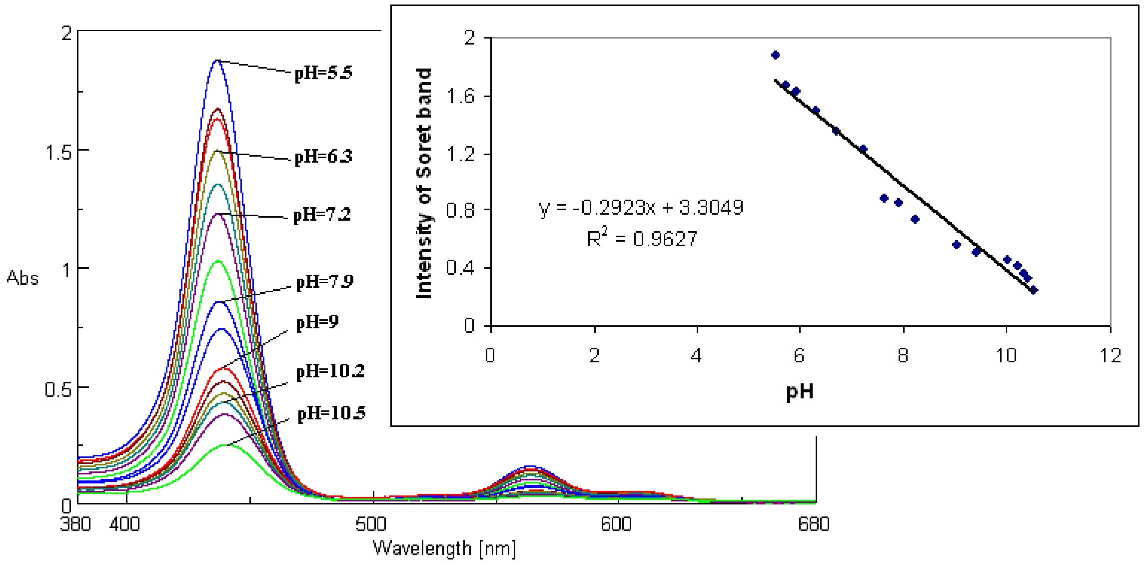

Fig. 4. The dependence between the intensity of absorption of ***Zn-TNMPyP*** *Soret band and the pH of the environment*

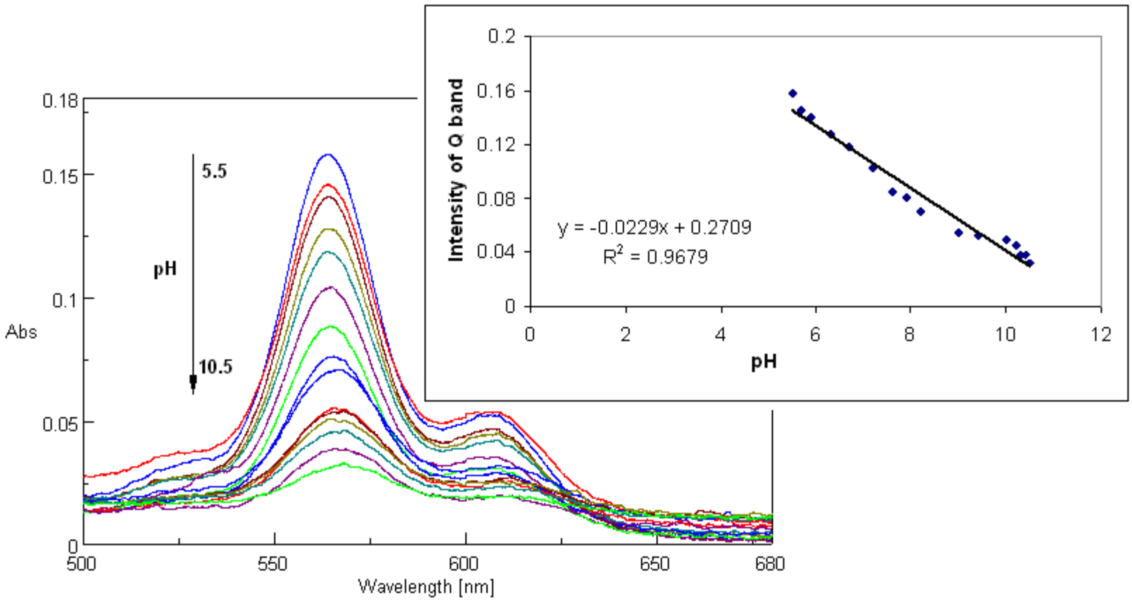

Fig. 5. The dependence between the intensity of absorption of ***Zn-TNMPyP*** *Q(0,1) band and the pH of the environment.*

By increasing the value of pH it is also to be noticed a slight bathochromic shift of the Soret band from 436.7 nm up to 440.45 nm occured (Figure 6). This is accompanied by the same effect regarding Q (0,1) band which is red shifted from 563.8 nm to 568.15 nm. Instead, the variation of the position of Q(0,0) band is haotic.

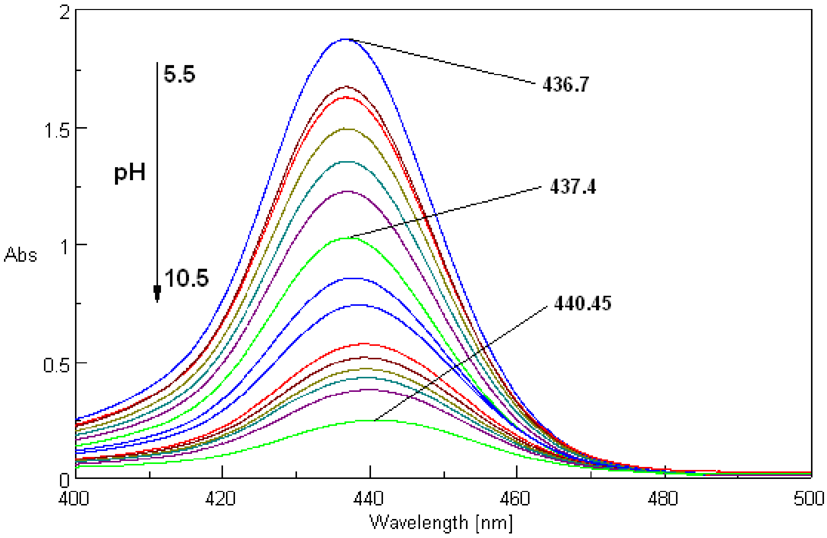

Fig. 6. The bathochromic shift of the Soret bands of ***Zn-TNMPyP*** *by increasing of pH*

4. Conclusions

This work put the basis for a rapid on-site real-time method for pH determination in water solution. It was demonstrated the potential of a water soluble metalloporphyrin, 5,10,15,20-tetrakis(N-methyl-4-pyridyl)porphyrin-Zn(II) tetrachloride to be an optical pH sensor in the 5.5-10.5 domain, in the UV-vis spectral range. The accuracy is 0.03 pH unit. Further work will be done to increase the confidence index in order to develop a non-glass porphyrin-based pH optical sensor for use in complex system.

Acknowledgement

Part of this work was supported by the Core Program PN 09-450102.

References

[1] D. Vlascici, E. Fagadar-Cosma, O. Bizerea-Spiridon, Sensors **6**(8), 892 (2006).
[2] D. Vlascici, O. Bizerea-Spiridon, E. Făgădar-Cosma, J. Optoelectron. Adv. M. **8**(2), 883 (2006).
[3] S. D. Starnes, S. Arungundram, C. H. Saunders, Tetrahedron Lett. **43**, 7785 (2002).
[4] X. Zhu, S. Fu, W.-K. Wong, W.-Y. Wong, Tetrahedron Lett. **49**, 1843 (2008).
[5] J. S. Hu, Y. G. Guo, H. P. Liang, L. J. Wan, L. Jiang, J. Am. Chem. Soc. **127**, 17090 (2005).
[6] C. Enache, E. Fagadar-Cosma, I. Armeanu, Z. Dudas, C. Ianasi, M. Vasile, D. Dascalu, Digest Journal of Nanomaterials and Biostructures **5**, 683 (2010)
[7] Z. Deyl, I. Miksik, A. Eckhardt, V. Kasicka, V. Král, Curr. Anal. Chem. **1**, 103 (2005).
[8] R. McDonald, N. Franssen, G. P. M. van Klink, G. van Koten, J. Organomet. Chem. **694**, 2153 (2009).
[9] Y.-Q. Weng, Y.-L. Teng, F. Yue, Y.-R. Zhong, B.-H. Ye, Inorg. Chem. Commun. **10**, 443 (2007).
[10] S. S. Bozkurt, S. Ayata, I. Kaynak, Spectrochim. Acta A **72**, 880 (2009).
[11] J. Spadavecchia, G. Ciccarella, P. Siciliano, S. Capone, R. Rella, Sensor. Actuat. B-Chem. **100**, 88 (2004).
[12] E. Fagadar-Cosma**,** C. Enache, I. Armeanu, G. Fagadar-Cosma, Digest Journal of Nanomaterials and Biostructures **2**, 175 (2007).
[13] S. Grama, N. Hurduc, E. Fagadar-Cosma, M. Vasile, E. Tarabukina, G. Fagadar-Cosma, Digest Journal of Nanomaterials and Biostructures **5**, 959 (2010).
[14] I. D. Şimăndan, M. Popescu, A. Lőrinczi, A. Velea, E. Fagadar-Cosma, Digest Journal of Nanomaterials and Biostructures **5**, 1029 (2010).
[15] T. Ohyama, H. Mita, Y. Yamamoto, Biophys. Chem. **113**, 53 (2005).
[16] F. M. Engelmann, P. Losco, H. Winnischofer, K. Araki, H. E. Toma, J. Porphyr. Phthalocya. **6**, 33 (2002).
[17] P. Hambright, T. Gore, M. Burton, Inorg. Chem. **15(9)**, 2314 (1976).
[18] S. L. Bailey, P. Hambright, Inorg. Chim. Acta **344**, 43 (2003).
[19] Y. Ishikawa, N. Yamakawa, T. Uno, Bioorgan. Med. Chem. **15**, 5230 (2007).