COMPARATIVE OPTICAL STUDY OF THE EFFECT PRODUCED BY AMINE HETEROCYCLES AS AXIAL LIGANDS FOR Zn-PORPHYRIN

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Abstract

The recognition of heterocyclic amines and their possible capture from polluted waters by porphyrins represents an ecological challenge. A novel metalloporphyrin bearing a pyridine functional group, Zn (II)-4-pyridyl-tris-(4-phenoxyphenyl) porphyrin (***Zn-PyPPP***), with high steric hindrance, whose base ligand was synthesized and characterized in our group, was used for a comparative study in order to investigate how the substituent -CH_3 group of 1-methyilimidazole would influence the access of the free nitrogen atom to the Zinc atom of the porphyrin, in comparison to pyridine, despite the fact that the whole molecule is smaller than the six-membered cyclic compound. As expected, the performance is lower by using 1-methylimidazole.The formed complexes were also morphologically studied by means of AFM measurements.

Keywords: Metalloporphyrin, heterocyclic amines, UV-vis spectrometry, AFM imaging

1. INTRODUCTION

Metalloporphyrins have the capacity to coordinate axial ligands, this property being essential in photosynthesis, enzymatic and catalytic processes [1]

The donor molecules that act as axial ligands have a significant influence upon the absorption properties of metalloporphyrins, modifying the shape, position and intensity of the absorption bands. The binding of several amine ligands to zinc porphyrins was studied [2] showing that a pre-organized structure of the Zn- porphyrin binding pocket is necessary to link the amine ligands. Zn- porphyrins were intensively used in the molecular recognition of aliphatic amines by analyzing the changes regarding the luminescence properties. Attempts to probe the ability of Zn-porphyrins to recognize certain biologically relevant drugs containing amine moieties were already reported [3]. Nevertheless there is a lot of interest regarding the recognition of heterocyclic amines [4].

Pyridine is a basic six membered N-heterocyclic compound (**Figure 1a**). It acts as nitrogen donor ligand and forms many metal-pyridine complexes and does not absorb in the visible-wavelength region (over 400 nm). [5]. Stable metal-ligand complexes are reported between pyridine and metalloporphyrins, producing a red shift of the Soret band of the porphyrin in the UV-vis spectrum [6].

Another N-substituted five membered N-heterocyclic compound, 1-methylimidazole, (**Figure 1b**), received our interest to use as axial ligand for Zn-porphyrins and has no remarkable peaks in the UV-vis spectrum in the work domain of interest 380 - 650 nm. The -CH_3 substituent at one of the nitrogen atoms may influence the access of the other nitrogen atom of amine molecule to the Zinc atom in the Zn-porphyrin in order to form the Zn-Porphyrin:1-methylimidazole complex as axial ligand.

A comparative study was performed in order to investigate how the -CH_3 substituent of 1-methylimidazole would influence the access of the free nitrogen atom to the Zinc atom of the porphyrin, in comparison to pyridine, despite the fact that the whole molecule is smaller than the six-membered cyclic compound. The porphyrin of choice, bearing a pyridine functional group, was Zn(II)-4-pyridyl-tris-(4-phenoxyphenyl) porphyrin (***Zn-PyPPP***), that is a novel compound, with high steric hindrance, whose base ligand was synthesized and characterized in our group [7] (**Figure 1c**).

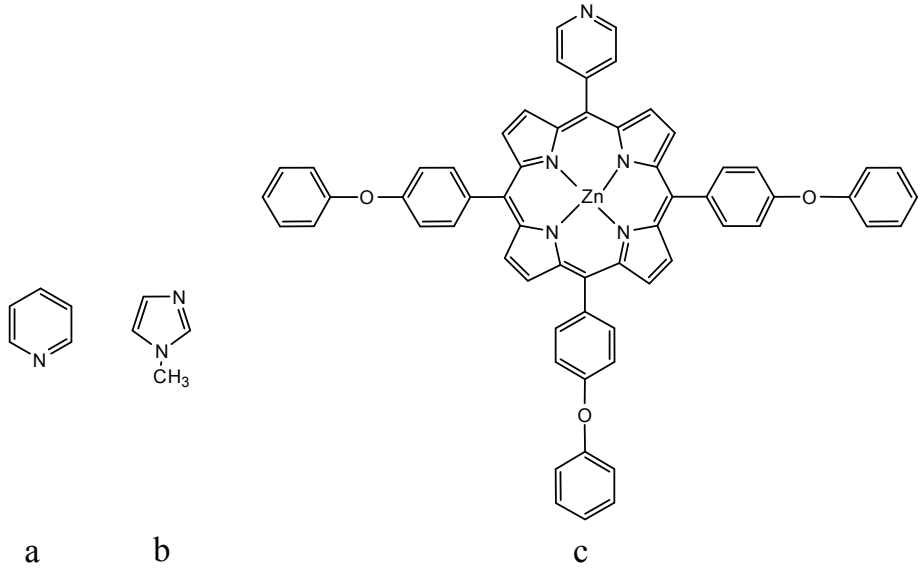

Figure 1 Structure of the investigated compounds

2. MATERIALS AND METHODS

The UV-vis spectra were recorded on a JASCO spectrometer model V-650. Atomic force microscopy (AFM) images were recorded on a Nanosurf®EasyScan 2 Advanced Research AFM (Switzerland) microscope. The samples were deposited from benzene onto pure silica plates and the surface imaging was performed at room temperature.

Benzene, DMF, pyridine and 1-methylimidazole were purchased from Merck and were used without any further purification. Zn(II)-4-pyridyl-tris-(4-phenoxyphenyl) porphyrin (***Zn-PyPPP***) was prepared by the metalation of the porphyrin base in DMF, at reflux, with 10 fold excess $Zn(CH_3COO)_2$ salt solved in methanol.

General procedure for spectroscopic measurements: Solutions in benzene of ***ZnPyPPP***, pyridine (c = 1 x 10^{-4} M) and of 1-methylimidazole (c = 1 x 10^{-3} M) were investigated. To 3 mL of ***ZnPyPPP*** solution in benzene were added portions of 40 µL amine solution in benzene; the mixture was stirred for 30 seconds and the UV-vis spectra were recorded for each step.

3. RESULTS AND DISCUSSION

Our attempt was to test if lower concentrations of pyridine or 1-methylimidazole can dissociate the associated metalloporphyrin molecules in benzene (at a concentration of 10^{-4} M) [6], but it resulted only in the confirmation of coordination of pyridine to the porphyrin moiety (**Figure 2**), as the Soret bands of the treated porphyrin did not decrease in enlargement. Both the Soret and the Q bands were only shifted to higher wavelengths. The decrease of the intensity of the shoulder located at 410 nm in close proximity of the Soret band can be indicative of the slow process of dissociation of the aggregated porphyrin molecules under the influence of pyridine adding. It can be observed that QII band is steadily decreasing in intensity, but the QI band is presenting an increase in intensity, due to changes in electron transfer.

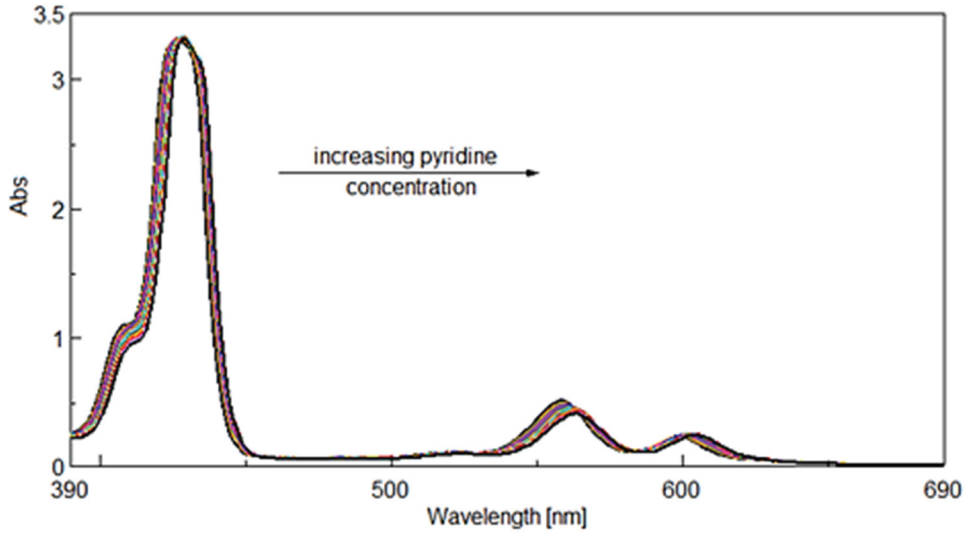

Figure 2 Concentrated ***Zn-PyPPP*** in benzene treated with diluted pyridine solution

A completely distinct purpose was focused on a more dilute porphyrin solution (c = 10^{-6} M), where the porphyrin is molecularly dissolved. In this second case, upon pyridine addition a Zn-porphyrin-pyridine complex was formed and justified by the presence of an isosbestic point on the Soret band at 433 nm in the UV-vis spectra (**Figure 3a**). This complex is stable for a large pyridine concentration domain, from 10^{-6} M to 10^{-5} M. The red shift of the Soret band can easily be observed from 427 nm in the spectrum of the sole ***Zn-PyPPP*** solution to 431 nm for a concentration in pyridine of 1.07 x 10^{-5} M. Beyond this pyridine concentration, the position of the maximum peak is preserved and only the decrease in intensity can be noticed. A linear dependence between the intensity of absorption at this wavelength with the pyridine concentration is observed and characterized by an excellent correlation coefficient of 99.55% (**Figure 3b**).

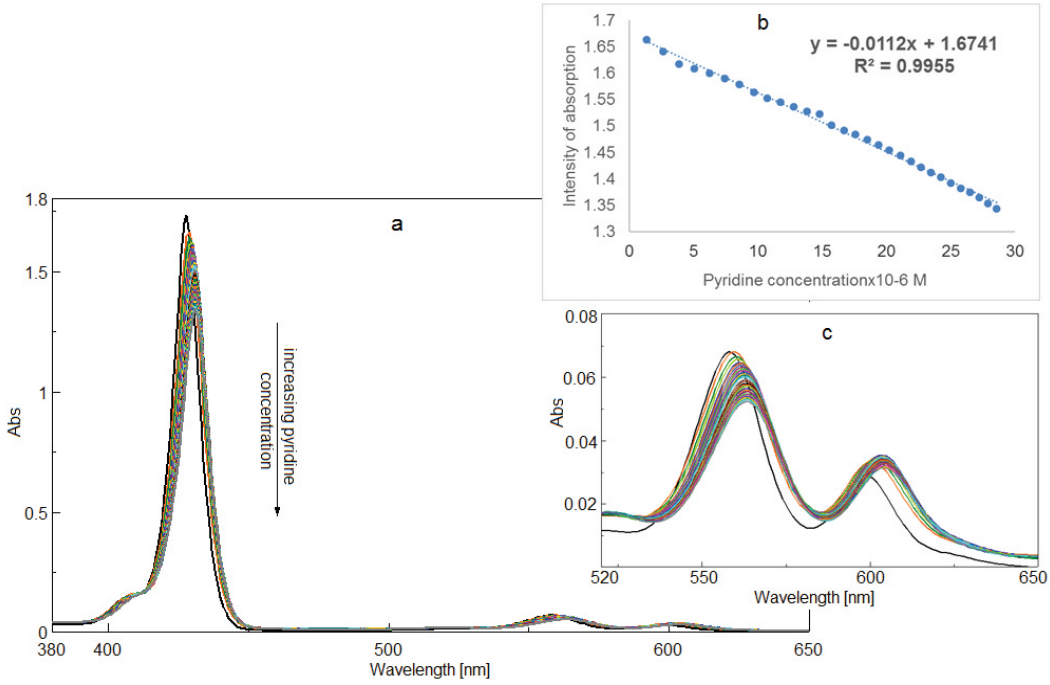

Figure 3 The superposed UV-vis spectra for successive adding of pyridine solution to dilute ***Zn-PyPPP*** solution (a); the linear dependence between the intensity of the Soret band and the pyridine concentration (b); details of Q bands (c)

It can also be noticed that the Q bands are initially shifting to higher wavelengths (**Figure 3c**), from 558 nm for QII in the metalloporphyrin spectrum to 563 nm for a concentration in pyridine of 1.07 x 10^{-5} M. After this concentration, the wavelength of the QII band stays the same. The QI band is of lower intensity and its peak is also shifting from 599 nm in the porphyrin spectrum to 604 nm for the same pyridine concentration and then it behaves the same as QII.

In case of 1-methylimidazole, the concentration domain for detection started one order of magnitude higher, from 10^{-5} M to 10^{-4} M (**Figure 4a**). The red shifting of the Soret band with the increase in 1-methylimidazole concentration is visible: from 427 nm in the bare ***Zn-PyPPP*** solution in benzene to 431 nm for a concentration in 1-methylimidazole of 1.105 x 10^{-4} M. Beyond this concentration only the linear decrease of the intensity with the increase in 1-methylimidazole concentration can be noticed, but the correlation coefficient is only 98.65% (**Figure 4b**), that is according to our presumption of -CH_3 group inducing higher steric hindrance.

The behavior of the QI and QII bands is similar to the case mentioned above (**Figure 4c**). The red shifting of the QII from 558 nm in the bare ***Zn-PyPPP*** solution in benzene to 563 nm for a concentration in 1-methylimidazole of 2.42 x 10^{-4} M, beyond which only a decrease in intensity is noticed. The shifting of the QI band continues in this case for a larger concentration domain, from 599 nm in the bare porphyrin spectrum to 606 nm for a concentration in 1-methylimidazole of 2.99 x 10^{-4} M.

Studying the AFM images recorded for the ***Zn-PyPPP*** after exposure to heterocyclic amines, it can be observed that the morphology of the particles is completely different. In the case of pyridine (**Figures 5a** and **b**) the triangular particles are well oriented, highly aggregated both in H and in J type forming stratified multiple layers, whereas in the case of 1-methylimidazole (**Figures 5c** and **d**) the triangles are no longer visible, the particles are largely associated in straw-like aggregates. Expectations to any crystallinity, in this second case, are annulled.

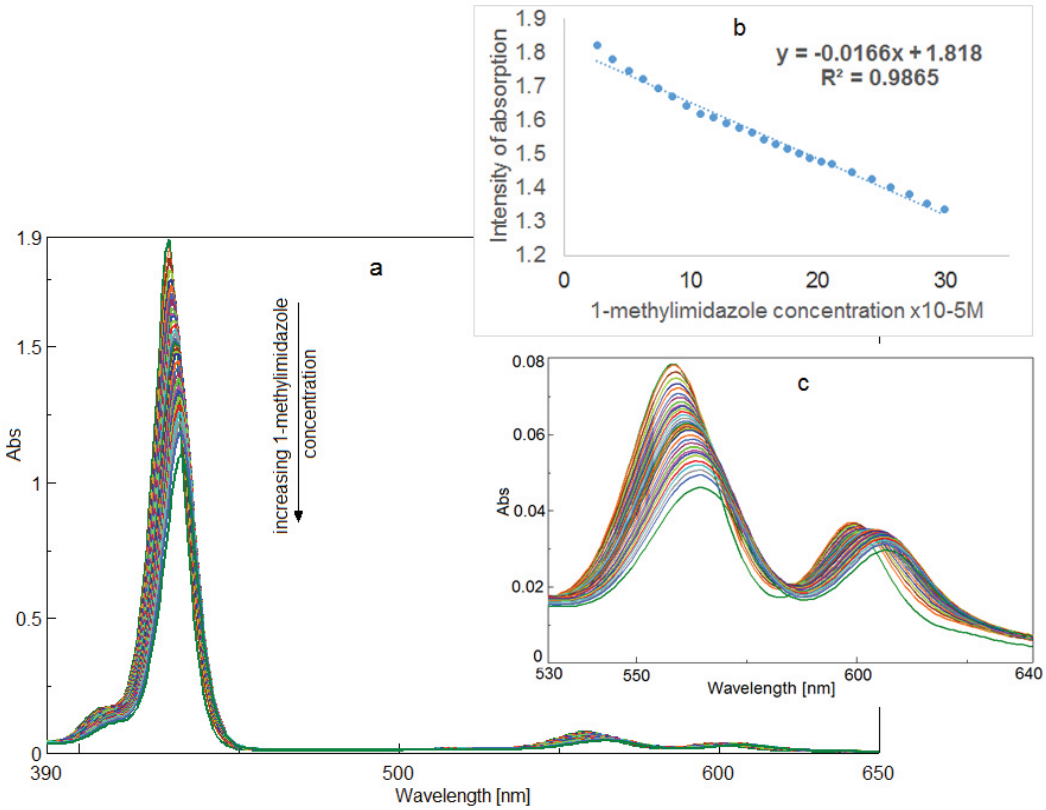

Figure 4 Superposed UV-vis spectra for adding increasing concentrations of 1-methylimidazole to ***Zn-PyPPP*** solution in benzene (a); the linear dependence between the intensity of the Soret band and the 1-methylimidazole concentration (b); details of the Q bands (c)

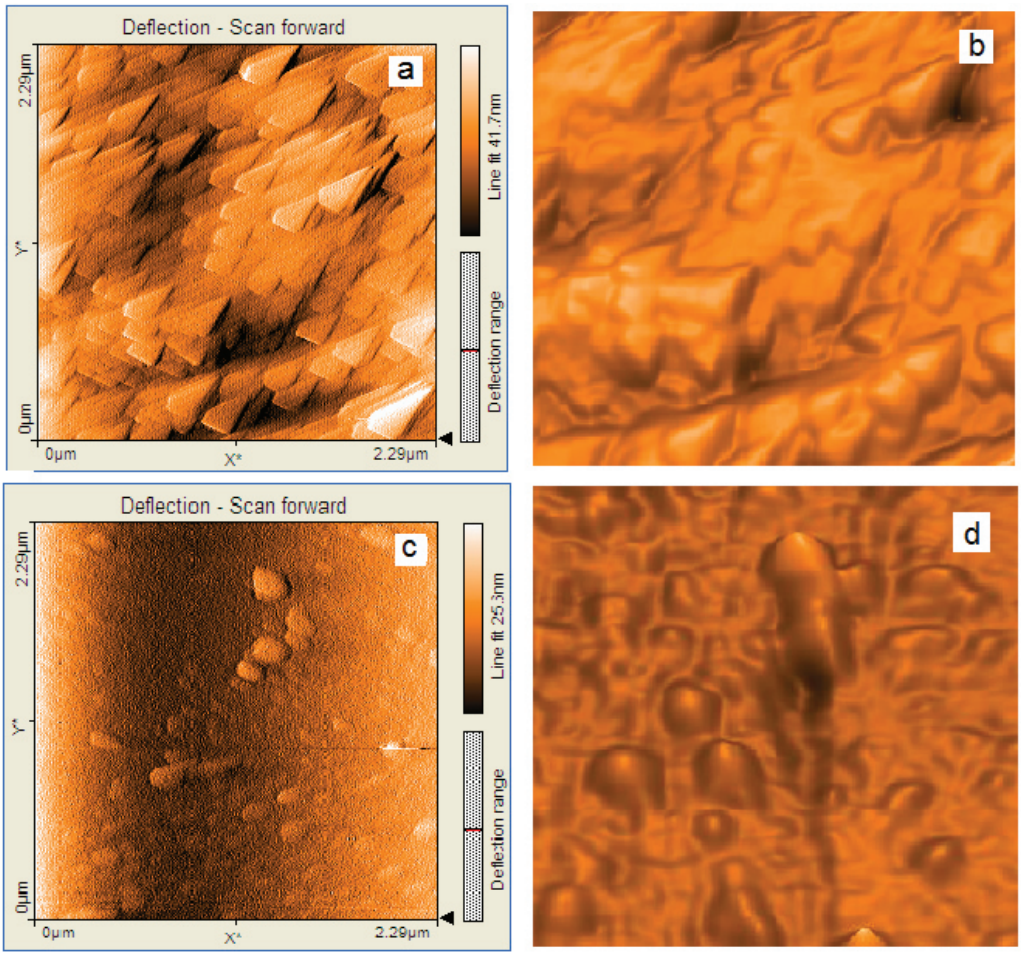

Figure 5 2D-AFM images for 2 micrometers of ***Zn-PyPPP*** treated with pyridine (a); and with 1-methylimidazole (c); 3D-AFM image in detail for ***Zn-PyPPP*** treated with pyridine (b); and with 1-methylimidazole (d)

4. CONCLUSION

This study confirmed the binding capacity of a novel derivative of Zn- porphyrin for axial ligation of heterocyclic amines. It can be concluded that the smaller, but more sterically hindered 1-methylimidazole molecule has a more difficult access to the Zn central ion of the *Zn-PyPPP* metalloporphyrin molecule in order to become an axial ligand and generate a complex, as compared to the six membered heterocycle of pyridine that has no substituents to hinder its access to the Zn atom. As a further purpose we will try to capture toxic amines from polluted waters.

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