

Electrochemical and Spectroscopic Studies of 5,10,15,20-Tetrakis(4-hydroxyphenyl)-21H,23H-porphine

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Abstract: The synthesis, spectroscopic and electrochemical characterization of 5,10,15,20-tetrakis(4-hydroxyphenyl)-21H,23H-porphine (THPP) is presented. THPP is also characterized by mass spectrometry in addition to a variety of spectroscopic techniques (UV-vis, FT-IR, fluorescence) and ¹H-NMR spectroscopy. Voltammetric and corrosion studies were carried out in order to investigate the electroactivity of THPP. Cyclic voltammograms obtained on Pt electrode, in PhCN with Bu₄NClO₄, present one reversible and two irreversible oxidation peaks. The corrosion inhibiting ability of THPP was illustrated by potentiodynamic curves obtained on carbon steel in 1N H₂SO₄, indicating a decrease of the current in the active region of the anodic polarization curve.

Keywords: 5,10,15,20-tetrakis(4-hydroxyphenyl)-21H,23H-porphine, fluorescence spectra, cyclic voltammetry, corrosion inhibition.

1. Introduction

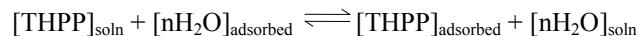
Porphyrinic molecules are capable of important changes concerning their properties by reconfiguring the electron distribution of the aromatic ring in order to develop supramolecular structures, thus allowing the accomplishment of some major objectives related to the development of fundamental sciences (physics and chemistry), nanotechnologies, highly strategically technology domains (photovoltaic cells), safety and durability for building engineering (corrosion inhibition), monitoring the quality of the environment (electrochemical sensors) and competitive health treatments (PDT therapy of cancer).

Porphyrins are known as substances with a great capability to form highly stable metallic complexes having a great potential as corrosion inhibitors. Their planar molecules containing four pyrrole subunits present bonding sites for complexes formation at the nitrogen atoms. The whole molecule structure shows conjugated double bonds due to the –CH= bridging groups and thus, a very mobile electronic system. These properties are very important in the adsorption process of these compounds on diverse metals surfaces.

5, 10, 15, 20 – Tetrakis (4-hydroxyphenyl) – 21H ,23H -porphine (THPP) is supposed to be a mixed inhibitor [1]. The adsorption of THPP occurs as a result of electrostatic forces between the electric charge on the metal and the high polarisability of the organic substrate molecule. The interaction of THPP with the metal interface, covered with oxides and water molecules, is even more favored by the

presence of the four hydroxyl groups in the *para* positions of the phenyl meso-substituents.

When iron is immersed in an aqueous phase, water molecules adsorb on its surface. Porphyrin molecules are adsorbed in their turn, by replacing the water molecules, this being considered the first step of metal-porphyrin interaction:



In a second step, THPP, in its adsorbed state, can form a Fe(II) coordination complex with the Fe²⁺ ions located on the metal surface, these compounds having a corrosion inhibitor activity given by both their high stability and low solubility in solution.

This paper presents the main results, which have been obtained by studying the electrochemical and spectroscopic behaviour of THPP.

2. Experimental

Apparatus

UV-visible spectra were recorded on a UV/VIS PERKIN ELMER, LAMBDA 12 spectrometer. FT-IR spectrum was registered on a JASCO 430 apparatus as KBr pellets. ¹H-NMR spectrum was registered on a 400 MHz Bruker spectrometer in CDCl₃ and chemical shifts are reported relative to internal TMS. The HPLC analysis was performed on a JASCO apparatus equipped with NUCLEOSIL C18 nonpolar column, and on KROMASIL SI 100 5um polar column, 240x4 mm with MD 1510

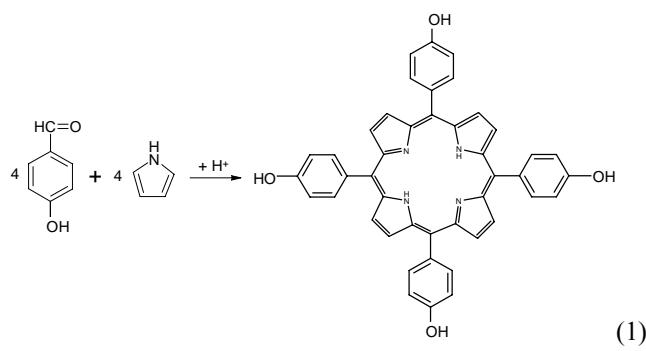
detector, at ambient temperature. The samples were subjected to analysis ($20\text{ }\mu\text{l}$) at a flow rate of 1 ml/min with methanol as eluent for the nonpolar column and hexane as eluent for polar column. A 212 Varian Finnigan Mat mass spectrometer was used for registering MS. The EI ion source conditions were: electron energy 54 eV , temperature up to $300\text{ }^{\circ}\text{C}$, mass range: $30\text{--}818$.

Voltammetric studies were made using a three-electrode cell and a potentiostat VOLTALAB PGZ 301 Dynamic – ETS Voltammetry – Radiometer Copenhagen with a VoltaMaster 4 program, at room temperature. The working electrodes were carbon steel (for corrosion inhibition studies) and platinum (for cyclic voltammetry). Counter electrode and reference electrode were always platinum and SCE. Other experimental specifications are given at the proper locations.

Reagents

Reagents were *p.a.* grade and were purchased from Fluka, Aldrich and Merck and used as received, excepting pyrrole distilled prior to use.

Synthesis and purification of 5,10,15,20-tetrakis (4-hydroxyphenyl)-21H,23H-porphine, (THPP) was done by Adler method. The porphyrin (THPP) was prepared according to modified literature methods [2-4], as figured in equation (1):



3. Results and discussion

The main physico-chemical characteristics of THPP were previously reported [5].

The UV-vis spectrum of THPP in THF (Fig. 1) is similar with the spectra registered in hexane and CHCl_3 , with the exception that no shoulder red shifted to Soret band, located near 450 nm is present, meaning that no aggregation process is to be noticed in this solvent.

The characteristic absorptions of porphyrin free-base are displayed in UV-vis spectrum of the studied compound, as presented in Fig. 1, with a typical Soret band and the four Q-bands in the visible region. The band around 419 nm was assigned to the Soret band, which arose from transition of $a_{1u}(\pi)\text{--}e_g^*(\pi)$, and the other four absorption maxima around 515 , 550 , 593 , and 650 nm could be attributed to the Q bands corresponding to $a_{2u}(\pi)\text{--}e_g^*(\pi)$ transitions.

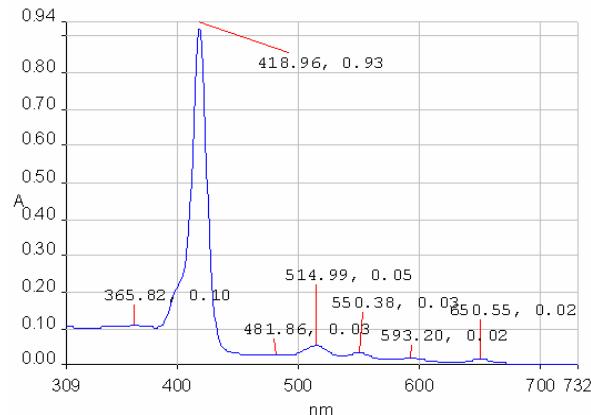


Figure 1. The UV-vis spectrum of THPP in THF.
 $\lambda_{\max}(\log \epsilon)$: $418.96(4.92)$; $514.99(3.65)$; $550.38(3.43)$;
 $593.20(3.25)$; $650.55(3.25)$

Regarding the $^1\text{H-NMR}$ spectrum of THPP, the internal proton (N-H) signals of porphyrin were located at the highest field region (-2.81 ppm) because of the ring current interaction. The other peaks, corresponding to phenyl and pyrrole protons or to OH are resonating in low field region of 7.36-8.11 ppm (*ortho*- and *meta*- H-Ph), 8.98 ppm (β -H-pyrrole), respectively to 10.01 ppm (OH).

The FT-IR spectrum of THPP, Fig. 2, is in complete agreement with the structure. The absorption band of strong intensity located at 3415 cm^{-1} is assigned to O-H stretching vibration and the absorptions at 3317 and 967 cm^{-1} are attributed to stretching and bending vibrations of N-H and C-N, respectively, which are the characteristic absorptions of porphyrin free base. The bands in the range 1500 - 1600 cm^{-1} are due to stretching vibration of C=C in the benzene aromatic ring.

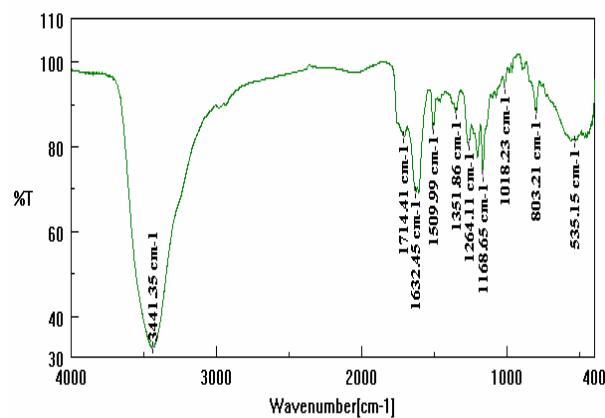


Figure 2. The FT-IR spectrum of THPP, KBr pellet

MS spectrum [6] of THPP (Fig. 3) can be commonly characterized by the presence of the molecular ion (M^+) at m/e value of 678 , by the existence of an $m/e=307$ fragment, corresponding to the doubly charged ion of the *meso*-tetraphenylporphyrin fragment, and by the loss of water molecules and the appearance of remarkable abundant (55%) carbonylum fragments ($m/e=94$).

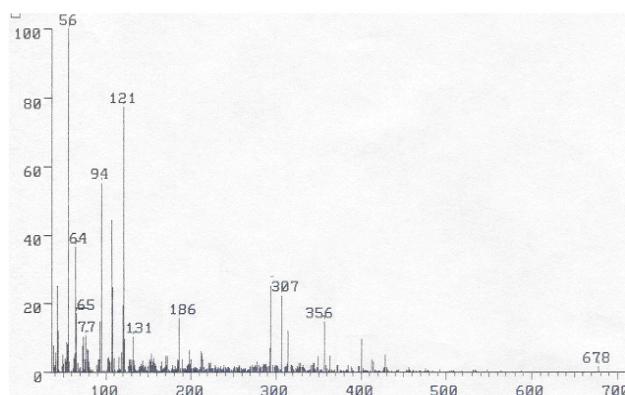
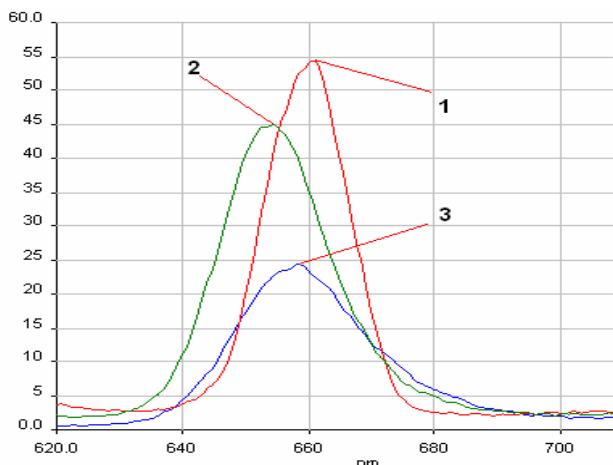


Figure 3. The mass spectrum of THPP

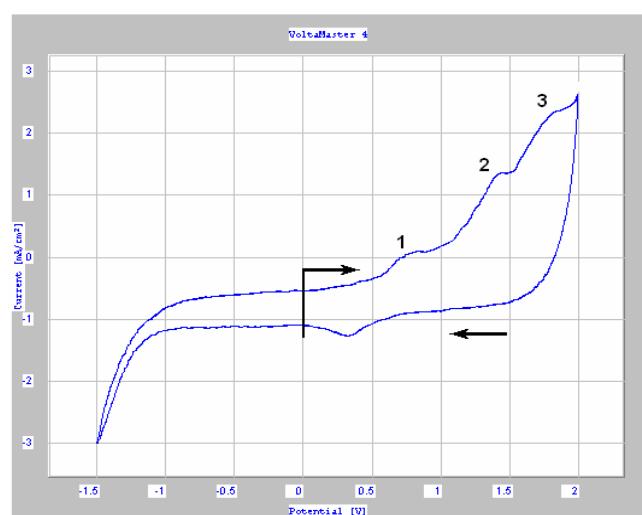
Fluorescence study gave the expected results, this compound being a well-known sensitizer. In Fig. 4, it can be seen the dependence of the emission maximum with the energy of excitation. When the emission spectrum is registered at a higher excitation energy, the emission has an increased intensity, and is red shifted (curve 1). With the decrease of energy of excitation (increase of λ_{ex}), the curves of emission have a significant smaller intensity (curve 3).

Figure 4. The superposed emission spectra of THPP at different wavelengths of excitations: $\lambda_{ex}=330\text{nm}$ (1); 405 nm (2); 440 nm (3). $c=1.11\times 10^{-5}\text{M}$.

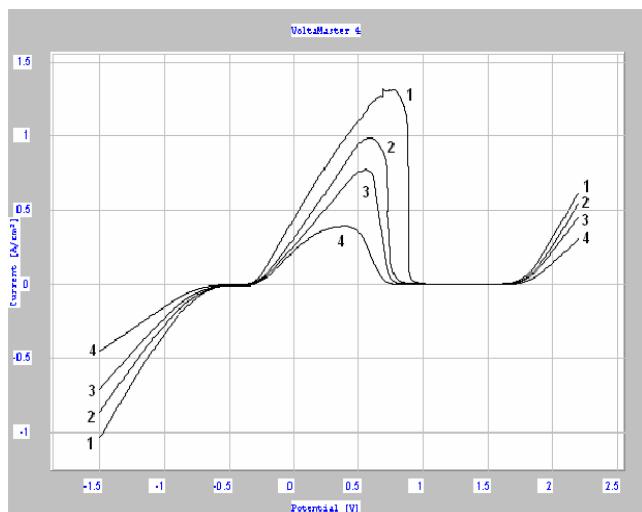
The voltammetric investigations on HTPP, Fig. 5, revealed the existence of a reversible oxidation step followed by two irreversible anodic peaks. These oxidation processes are explained by the formation of π -cation radicals and dications. The potential values for the mentioned anodic peaks are given in Table 1, and are in agreement with the reported data [7].

TABLE 1. Reaction potentials for THPP according to the voltammogram from Fig. 5.

ε_{pa} (V/SCE)	0.80	1.40	1.80
ε_{pc} (V/SCE)	0.30		
$\varepsilon_{1/2}$ (V/ESC)	1.60		
Step	1	2	3

Figure 5. Cyclic voltammograms of THPP
(Pt electrodes, PhCN, 0.1 M Bu_4NClO_4 , scan rate 0.5 V/s, ref. SCE, 2 mM THPP, 25°C)

The corrosion inhibition of THPP was investigated on carbon steel in H_2SO_4 . The results are presented in Fig. 6 and demonstrate that THPP presents an important inhibition effect on the corrosion process of carbon steel. The decrease of the critical current density for passivation (in the active region) is significant, but there is also some influence as inhibitor in the transpassive region (the oxygen evolution) and on the cathodic hydrogen evolution reaction.

Figure 6. Potentiodynamic curves obtained on carbon steel in H_2SO_4 1N, scan rate 50 mV/s. THPP conc., mM: without THPP (curve 1), 0.05 (2), 0.1 (3) and 0.2 (4).

4. Conclusions

The porphyrinic compound, namely 5,10,15,20-tetrakis(4-hydroxyphenyl)-21H,23H-porphine (THPP) was synthesized and analyzed. The main spectroscopic properties are presented and discussed and are in total agreement with the general properties of porphyrins. The allure, position and intensity of the emission spectra of THPP are strongly

dependent on the wavelengths of the excitation signal. THPP presents electrochemical activity. It is oxidized on platinum electrode, in nonaqueous medium, at three different potentials (three electrode reaction steps), as expected from related proppyrins. From the influence on the passivation curve of carbon steel in H_2SO_4 , an important corrosion inhibition activity is to be noticed.

ACKNOWLEDGMENT

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