



Comparative study of the optical behavior of a porphyrin encapsulated in sol-gel silica coatings and in solution as a function of pH



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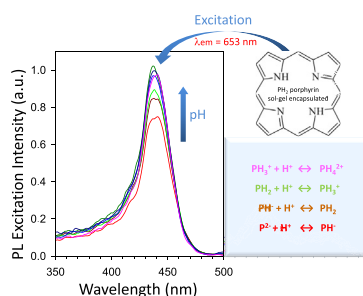
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HIGHLIGHTS

- Porphyrin-doped silica coatings were prepared by sol-gel.
- Films optical properties were studied and compared to the behavior of the molecule in solution.
- A quasi-linear behavior throughout the pH range studied was found.
- Luminescent emission peak and molar absorptivity were maximum at slightly lower wavelength than molecule in solution.

GRAPHICAL ABSTRACT



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ABSTRACT

We report a comparative optical spectral study as a function of pH on a porphyrin encapsulated in a sol-gel matrix and in methanol solution. Its response has been discussed in terms of pH-sensitivity as a function of the coatings thickness. Comparison with the behavior of such porphyrin in methanol solution is also included.

Optical properties of the porphyrin doped coatings show a quasi linear behavior throughout the pH range studied. Luminescent emission of doped coatings has its maximum peak at a slightly lower wavelength compared with the response in liquid medium (methanol solution), while in the excitation spectra no clear tendency was observed for different pH. Coatings doped with 1 wt% porphyrin fulfill Lambert-Beer law, although the molar absorptivity of the encapsulated porphyrin in the coatings is slightly lower than in methanol solution.

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1. Introduction

The sol-gel method is a low-cost chemical route which enables the encapsulation of organic molecules [1,2]. In many cases, such molecules preserve their properties once immobilized inside the

sol-gel material [3]. Cationic porphyrins and their metal complexes [4] attract significant attention because their structure makes them suitable candidates for optical and catalytic applications. For instance, due to their unusual luminescence, they have been applied for photosensitizers [5] and sensors [6–8], among others. In this respect, the molecules are preferably immobilized inside a porous network to obtain easy to use materials provided with a better applicability, photostability or chemical durability [9].

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However, the luminescence properties of many porphyrins are strongly affected by the particular structure of the porous matrix [10]. Therefore, a comparison study of the porphyrin molecules behavior in their free form and once encapsulated is necessary [8,11]. Other applications of the porphyrin selected in the present work can be found in: quantitative determination of cadmium [12], ascorbic acid determination [13], electrocatalysis [14], biomedical and biochemical applications [15–17], cationic clays [18] and new sol-gel materials for electrodes and optical sensors [19,20].

Among the different materials suitable for porphyrin immobilization, thin sol-gel coatings have proven to be optimum [21]. Sol-gel coatings advantages are well known: easy preparation at room temperature, low cost processing equipments, good mechanical adherence to the substrate (usually common glass slides), and aptitude of the sols to coat surfaces of different size, shape and geometry. The use of very pure chemical reagents such as alkoxides and/or alkylalkoxides of silicon, zirconium, aluminum, boron, etc., which constitute the coating matrix, ensures the purity and stability of the doped coating. Therefore, these sol-gel coatings are materials with good mechanical, thermal and optical properties, in addition to a chemical stability and adequate porosity [22]. This latter property is very interesting since the encapsulation of the dopant, in this case a porphyrin, depends on such porosity, which ensures the physical contact of the encapsulated dopant with other chemical species coming from the exterior.

The objective of this work is, on the one hand, the preparation of a porphyrin doped sol-gel silica coating and, on the other hand, the study of its optical behavior, both in an alcoholic solution and once encapsulated in the sol-gel coating. The porphyrin selected was 5,10,15,20-tetrakis (1-methyl-4-pyridil)-21H, 23H-porphyrin. The main aim of this comparison study is to clarify the porphyrin optical behavior under different environments, liquid and solid, and to point out similarities or differences related to other organic dopants also encapsulated in sol-gel thin coatings [23] to check their ability as potential optical material.

2. Experimental methods

Silica matrices of the thin coatings were prepared from a sol whose components were: silicon tetraethoxide (TEOS, $\text{Si}(\text{OC}_2\text{H}_5)_4$), hydrochloric acid HCl 3 M and methanol (MeOH) in molar ratio 1:4:8, and deionized water to accomplish stoichiometric TEOS hydrolysis. The first step consists on a pre-hydrolysis of the silicon alkoxide diluted with methanol and HCl 3 M, which catalyzes the reaction, at room temperature under constant stirring to warrant the sol homogenization. A methanol solution (1 wt % respect the final silica content of the sol) of the p-tosilate salt of the 5,10,15,20-tetrakis (1-methyl-4-pyridil)-21H, 23H-porphyrin (herein after the porphyrin, Fig. 1) was prepared and added to the pre-hydrolyzed TEOS solution, i.e. when the solution temperature increased spontaneously at about 5 °C from room temperature, as a consequence of the hydrolysis reaction heat release.

After 30 min of continuous stirring, the homogeneous sol was ready to be used for depositing thin coatings upon common soda lime silicate glass slides. Chemically cleaned glass slides were coated at room temperature by dip-coating into the sol at different constant rates in the 5–30 cm min^{-1} range. After drying 10 min at room temperature, the coated slides were heat-treated for 3 days at 60 °C in a forced air stove. Thicknesses of the doped coatings were estimated by means of the corresponding reflectance spectra (fringe method) and they vary in the 100–550 nm range.

Additionally, another porphyrin solution in a mixture of methanol and deionized water (volume ratio 1:4) was prepared. Aqueous phase was a pH buffered solution (pHydrion Buffers®, Micro Essential Laboratory Inc. USA), also used to analyze the

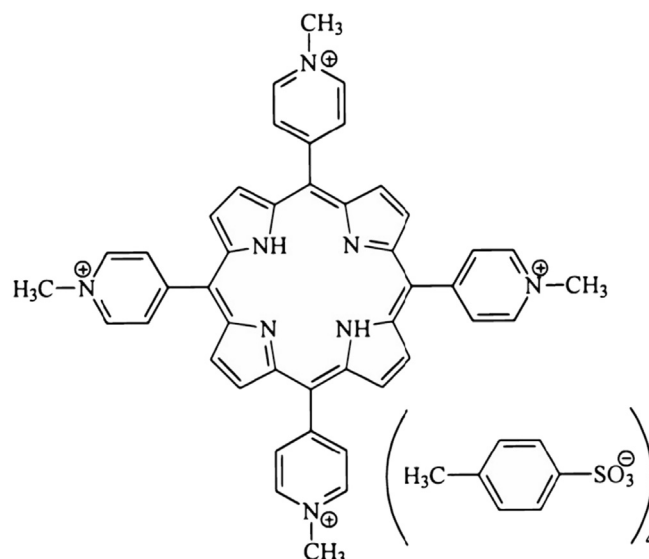


Fig. 1. Molecular structure of the porphyrin used as a dopant of the sol-gel thin coatings.

coatings behavior. The concentration of other porphyrin solutions ranged between 5.0×10^{-4} M and 3.0×10^{-5} M.

Optical absorption spectra of both solutions and coatings were recorded with a Shimadzu UV 3100 spectrophotometer provided with an integrating sphere. Solutions spectra were recorded in the wavelength range of 200–750 nm, while coatings spectra were recorded in the 280–750 nm range. Luminescence spectra (excitation and emission) were recorded with a Perkin-Elmer LS-5B fluorescence spectrometer. Excitation spectra of both solutions and coatings were recorded in the wavelength range of 230 nm to ~15 nm below the emission wavelength selected. Emission spectra were recorded from ~15 nm above the excitation wavelength selected up to 720 nm.

3. Results

Optical behavior of the porphyrin mentioned above has been studied in the 0–13.4 pH range in solution and encapsulated in the thin sol-gel coating, since both show sensitivity against pH changes. Solubility and chemical structure of the porphyrin molecule depend on the pH. The porphyrin macromolecule can be considered as an ampholyte with two pyrrolic nitrogen atoms able to accept protons, and two NH groups able to lose them (Fig. 2).

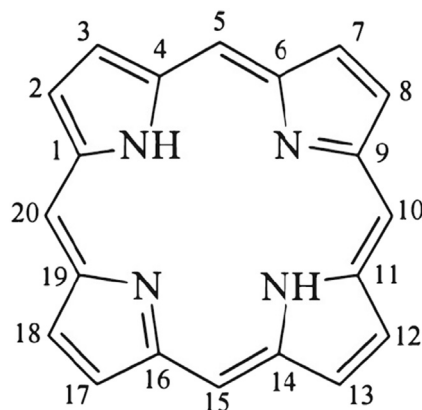


Fig. 2. Free base molecular structure of the porphyrin (PH_2).

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