

Ft-ir, fluorescence and electronic spectra for monitoring the aggregation process of tetra-pyridylporphyrine entrapped in silica matrices

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New inorganic-organic hybrid materials consisting in 5,10,15,20-tetra(4-pyridyl)-21H,23H-porphine (TPYP), encapsulated in silica matrices were obtained by the sol-gel process. A control of pH influence over accessibility of incorporation of porphyrin into silica was performed, by using two different acids in the first acid catalyzed step of the sol-gel process. As a novelty element, glacial acetic acid was used as catalyst, and the results were compared with those obtained with the commonly used HCl. The compositions were monitored and comparatively characterized by using spectroscopic methods such as FT-IR, UV-vis and luminescence. The major changes in UV-vis spectral shape might be attributed to the dication (H^+_2TPYP) generation, in acid media, and are associated with an increase of the intensity of the last Q band. Atomic force microscopy (AFM) investigations were carried out and discussed. Co-facial porphyrin aggregation with random orientation was noticed.

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1. Introduction

New state-of-the-art experimental approaches in physics and biophysics as well as applications in modern optoelectronic devices require a photosensitizer to be embedded on a solid matrix. The most used method for entrapping a meso-arylporphyrine is based on the reaction of its peripheral groups with complementary reactive groups of the surface matrix. The second method is relying on non specific adsorption phenomena. A random orientation of the immobilized photosensitizer is expected by using either of these methods [1].

In connection with previous studies concerning porphyrin incorporation in organic polymeric membranes [2,3], the aim of this contribution is to design a new hybrid material by entrapping 5,10,15,20-tetra(4-pyridyl)-21H,23H-porphine (TPYP) - structure is given in Fig. 1- into an inorganic silica matrix by means of two steps acid-base catalysis sol-gel process. The porphyrine (TPYP), molecules easily self-assemble into large highly ordered domains and their photophysical properties could be strongly affected by changes in their aggregation state. Among the many possible supramolecular interactions, π - π stacking have generated nanoaggregates based on porphyrins and metalloporphyrins with remarkable photophysical properties [4-6].

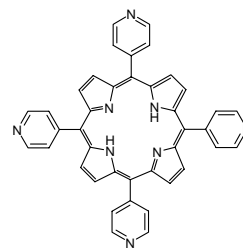


Fig. 1. Molecular structure of the 5,10,15,20-tetrapyridyl-21H,23H-porphine.

In order to optimize the immobilization process a control of pH influence over accessibility of incorporation of porphyrin into silica was performed by using two different acids in the first acid catalyzed step of the sol-gel process: hydrochloric acid and glacial acetic acid.

2. Experimental

Apparatus: FT-IR (JASCO 430 FT-IR, KBr pellets) spectra were carried out, in the 4000-400 cm^{-1} range. UV-visible spectra were recorded using a UV/VIS PERKIN ELMER, LAMBDA 12 spectrometer. 1H -NMR spectrum was registered on a 400 MHz Bruker spectrometer in $CDCl_3$ and chemical shifts are reported relative to internal TMS (0.0 ppm). The HPLC analysis were performed on a JASCO apparatus equipped with NUCLEOSIL C18 nonpolar column, and on KROMASIL SI 100 5 μm polar

column, 240×4 mm with MD 1510 detector, at ambient temperature. A 212 Varian Finnigan Mat mass spectrometer was used for registering MS. Fluorescence spectra were recorded in THF and in aqueous solution with an LS 55 PERKIN ELMER apparatus in a 1 cm cuvette.

Atomic force microscope (AFM) measurements were made with sample preparation onto a silica plate. Scanning probe microscopy investigations were carried out with an Atomic Force Microscope designed at Twente University of Holland. A Park Scientific microcantilever was used for performing measurements with a tip having a radius of curvature of around 20 nm. The measurements are performed quantitatively on the plane of the measurement and in the direction perpendicular to the surface with lateral resolution of 20 nm and of 2 nm vertically, on maximum of 20×20 μm area, the maximum admitted roughness of the samples being of 6 μm. Height image data obtained by the AFM is three-dimensional. The usual method for displaying the data is to use a colour mapping for height, for example black for low features and white for high features. All AFM measurements were done at ambient conditions (temperature: 21±2 °C; relative humidity: 50–70%).

Preparation of TPYP was done accordingly to literature data [7]: A mixture of 9.41 ml (100 mmol) of 4-pyridinecarboxaldehyde and 13 ml (100 mmol) propionic anhydride was dissolved in 300 ml propionic acid and 6.93 ml (100 mmol) pyrrole dissolved in 100 ml of propionic acid, was added dropwise to the mixture heated to reflux, for 1/2 h. The whole reaction mixture was refluxed for over 2 h. After cooling to room temperature, the solvent was evaporated to dryness, and the oily residue was repeatedly washed with hot water, neutralized by aqueous ammonia (25%), and washed again with hot water. The purple solids obtained by this procedure were filtered and dried. The dry solid material was treated with three portions of 80 ml of dichloromethane, each followed by filtration. To the combined organic phases, 15 g of basic alumina (Brockman activity grade II) were added, and the solvent was evaporated to dryness. Separation of TPYP was achieved by column chromatography, using as eluent a mixture of chloroform, dichloromethane and ethanol.

In situ two steps acid/base catalyzed sol-gel method, using HCl. A mixture of H₂O (2.40 g, 0.133 mol) and HCl 37% (0.066 g, 0.67 mmol) were added by slow dropping under vigorous stirring to a solution of TEOS (6.945 g, 0.033 mol) dissolved into EtOH (6.14 g, 0.133 mol). The following molar ratios were kept constant during the first acidic step: TEOS: EtOH: H₂O: HCl = 1: 4: 4: 0.02. After 15 minutes a violet solution of TPYP (0.0110 g, 17.7×10⁻³ mmol) dissolved into 30 ml THF was slowly added, and as a result a green solution is generated. The basic catalysis was controlled by slowly dropping of a total amount of 0.49 g NH₃ 2.5%. The final material was a transparent pink-red stable gel. After the wet gel was dried for 8 hours at 120°C, the colour turned into light red.

The control sample was identically synthesized, without porphyrin adding, and by using a total amount of 2.04 g solution of NH₃ 2.5%. A transparent gel was obtained.

In situ two steps acid/base catalyzed sol-gel method, using glacial acetic acid, was conducted in the same conditions, excepting that TPYP (0.002 g, 3.23×10⁻³ mmol) was dissolved into glacial acetic acid (7 g, 0.11 mol) and 10 ml THF. The final red gel was obtained after addition of 1.43 g NH₃ 2.5% to the initial green solution from the first step acid catalyzed sol-gel process.

The silica control sample was synthesized identically without porphyrin adding. Transparent gel was obtained after the addition of 3.09 g NH₃ 2.5%.

3. Results and discussion

The main spectrometric characteristics of free base porphyrin are previously reported by our team [8] and given below:

5,10,15,20-tetrakis(4-pyridyl)-21H,23H-porphine (TPYP) violet crystals, η = 11%, FT- IR(KBr), cm⁻¹: 3306.36; 3098.87; 3024.8; 1589.06; 1546.63; 1404.89; 1349.93; 1068.37; 975.80; 884.20; 798.38; 724.13; 656.64; 528.4. ¹H-NMR (CDCl₃, 400 MHz), δ, ppm: - 2.916 (s, 2H, NH), 8.155-8.169 (dd, 8H, 3,5 H- Ph (*meso*)), 8.873 (s, 8H, 2,6 H- Ph (*ortho*)), 9.062-9.076 (d, 8H, β-H). UV-Vis (MeOH) – λ_{max} (log ε): 411.96 (5.61); 509.00 (4.84); 537.99 (4.77); 584.11 (4.77); 642.00 (4.77). UV-vis (THF) -λ_{max} (logε): 415.04 (5.66); 511.03 (4.43); 543.34 (3.95); 587.95 (3.95); 642.95 (3.95).

The chemical structure of hybrid materials, of TPYP and silica control samples are characterized by FT-IR spectroscopy and exemplified, (Fig. 2), for *in situ* sol-gel method in acid-base catalysis. Both of the FT-IR spectra of the hybrid materials have the same allure. The FT-IR spectrum of TPYP, according to (Fig. 2, curve 1) presents the main absorptions at 3306 and 975 cm⁻¹ which are attributed to stretching and bending vibrations of N-H and C-N, respectively. The bands in the range 1500 - 1600 cm⁻¹ are due to stretching vibration of C=C in the pyridyl aromatic ring. The intense absorption band at 798 cm⁻¹ is attributed to the vibration of C-H bond from pyrrole.

Both spectra of silica control sample and porphyrin-silica hybrid materials, Fig. 2 (curves 2 and 3), exhibit a broad band between 3100 and 3750 cm⁻¹ related to the presence of Si-OH, and to the inter- and intramolecular hydrogen bonds; a band around 3000 cm⁻¹ is related to C-H bond. The only one difference between these two spectra can be noticed within the 1300 - 1000 cm⁻¹ region with respect to the wavenumber of the maximum of absorption (1087 cm⁻¹ and 1092 cm⁻¹ respectively).

The spectra of these two samples display intense absorption peaks at about 800, 950, 1070 and 1170 cm⁻¹. These absorption peaks are associated to the SiO₂ phase; they have been assigned to the absorption of Si-O-Si symmetric stretching, Si-OH group, transversal optic (TO) Si-O-Si asymmetric stretching and longitudinal optic (LO) Si-O-Si asymmetric stretching respectively [9,10].

The bonding modes near 1065 cm⁻¹ and 1105 cm⁻¹ can be assigned to the Si-O-C asymmetric stretching mode in a ring link and in an open link respectively.

The broad bonding mode at 1150 cm⁻¹ was attributed to the Si-O cage-like stretching mode. In the spectrum of hybrid material registered in this region, the bands of TPYP bending-groups were not clearly identifiable because they overlap with the broad bands of Si-O-Si and Si-O-C in hybrid material [11]. This supplementary feature [12] could indicate that silica component was, in some manner, bonded to the organic TPYP.

Only one difference is to be noticed in case of using as catalyst, glacial acetic acid, for obtaining the hybrid material. In the region between 1065 and 1300 cm⁻¹, the bonding modes of Si-O-Si and Si-O-C are more broadened, comparing to the synthesis using as catalyst HCl.

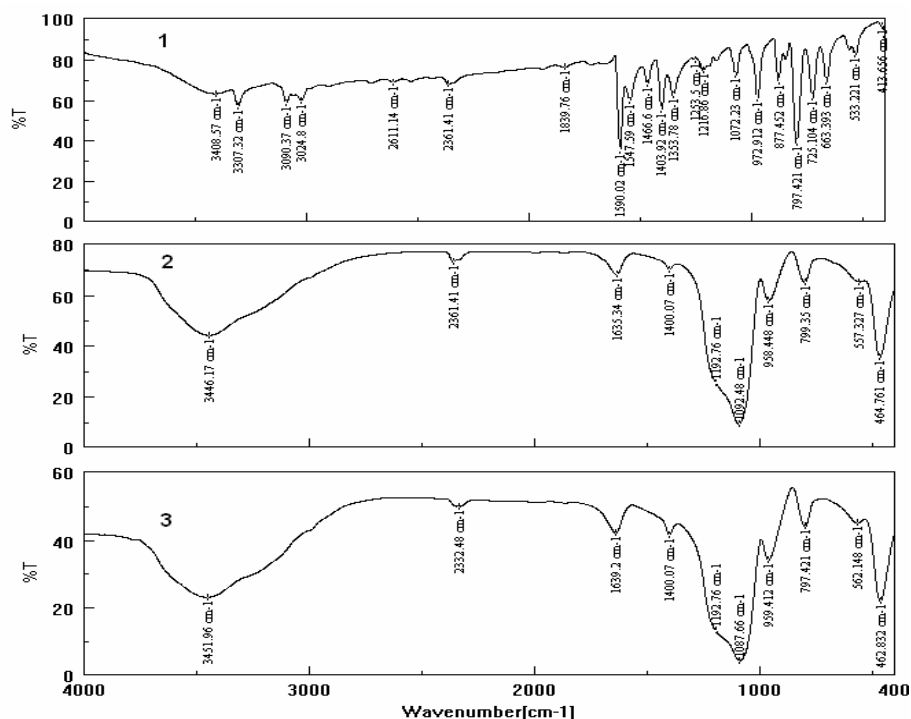


Fig. 2. FT-IR spectra of TPYP (curve 1), silica control sample (curve 2) and hybrid material (curve 3) In situ sol-gel method, in acid- base catalysis, using HCl.

The UV-vis spectrum of *meso*-tetrapyrrolylporphyrin (TPYP), registered in THF has the *etio* type shape (Fig. 3). The spectrum contains the high intensity Soret band, with maximum at 415 nm, followed by four Q bands, Y-polarized bands IV [$Q_{Y(0,1)}$] and III [$Q_{Y(0,0)}$] at 511 and 543 nm, respectively, and X-polarized bands II [$Q_{X(0,1)}$] and I [$Q_{X(0,0)}$] at 588 and 643 nm, respectively.

Meso-tetrapyrrolylporphyrin (TPYP) and its complexes are usually more stable to pH changes than the corresponding TPP analogues because of the relatively high pK of the pyridyl substituents. Two different steps of protonation are involved in this case; some protons may be attached to the external pyridyl nitrogens while other protons are bonded to the internal pyrrole nitrogens.

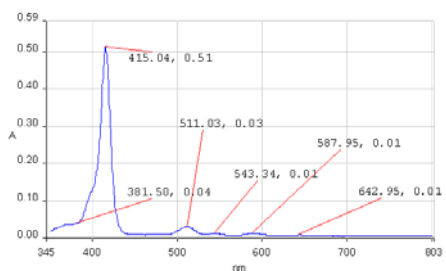


Fig. 3. UV-vis spectrum of TPYP in THF ($c=1.1 \times 10^{-6} M$).

At pH values below 3.5 the absorption spectrum of TPYP in the visible spectral region transforms into a two Q-band spectrum, composed of an intense absorption band at 654.14 nm, and a band at 601.74 nm of weaker intensity.

From Fig. 4, registered at pH=2, it can be seen that the Soret band is red-shifted with more than 41 nm, with respect to that of spectrum in organic solvents, being situated to 456 nm. In acid medium, the formation of the two paired porphyrin π -electrons in the aggregates, is concordant with the observed Soret band-shift and broadening in the UV-visible absorption spectrum of the aggregate [13].

With increasing acidity to pH=2 and lower, two additional protons bond to the nitrogen atoms in the center of porphyrin ring, so that the partial positive charge is induced in the central part of the molecule. These changes in spectral allure might be attributed to the dication (H_2^+TPYP) generation, and are associated with an increase of the intensity of the last Q band. Literature data offers information about similar changes in absorption spectra which can be induced by varying the ionic strength of acidic solution of porphyrins and have been assigned to the formation of aggregates [14, 15].

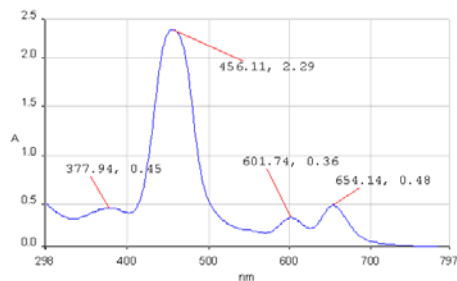


Fig. 4. The shape of the absorption spectra of emerald green TPYP-silica material in acid-catalyzed step by using HCl, at pH=2.

By using glacial acetic acid, the Q bands III and IV do not disappear but are very much decreased in intensity, as illustrated in Fig. 5.

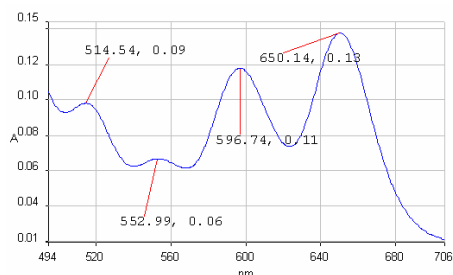


Fig. 5. A detail of the shape of the Q bands of green coloured TPYP-silica material during first acid step catalyze at pH=3.5, by using glacial acetic acid.

As a consequence of base addition, and the increase of the value of pH, the lower energy Soret band at 456 nm, associated with J type aggregate mode, decreases gradually, while the high-energy Soret band around 420 nm, associated with monomer, re-appears. [16],

The final allure of the Q bands of porphyrin entrapped in silica gel transforms from initial *etio* type, in which the intensity of Q bands are decreasing in the order: IV>III>II>I, to *phyllo* type in which the intensity of the Q bands are decreasing in the order: IV>II>III>I (Fig. 6).

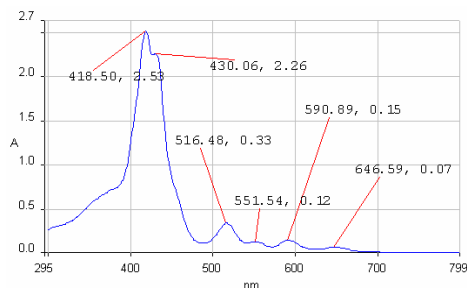


Fig. 6. The UV-vis spectrum of red hybrid TPYP-silica material at the gelation point during the final two step acid-base catalyzed process.

The slight splitting of the Soret band is providing that the dye molecules tend to aggregate also by π - π and hydrophobic interactions [17].

The emission spectra of TPYP-hybrid materials obtained by using into acidic step process HCl, respectively CH_3COOH , in comparison with silica matrix control sample, registered at λ excitation wavelength of 420 nm, are presented in Fig. 7, and each of them present two emission maxima at around 655 nm and at 715 nm.

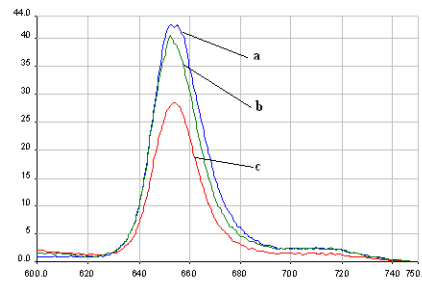
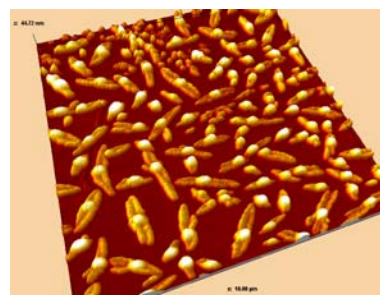
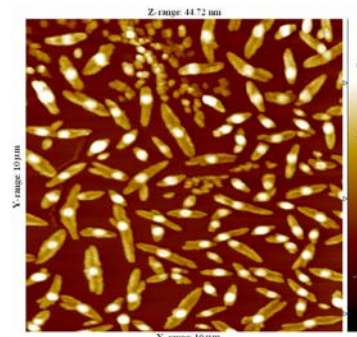


Fig. 7 Emission spectra of TPYP-hybrid material by using HCl (a), respectively CH_3COOH (b) in comparison with silica matrix control sample (c), at λ excitation wavelength: 420 nm.



(a)



(b)

Fig. 8. 3D (a) and 2D (b) AFM image-profile (10 x 10 μm) of the hybrid material obtained by entrapping of porphyrin within a silica matrix derived from a two steps acid/base sol-gel process, by using HCl.

The intensity of the emission is significantly increased in both hybrid materials in comparison with the silica matrix control sample, certifying that such materials, containing an organic dye, can be used in design of photocurrent generating hybrid devices in order to optimize light adsorption, surface binding, and charge

transfer, with expected efficiencies in building of solar cells.

3D and 2D AFM image-profile measurements of hybrid TPYP-silica material (Fig. 8) show that the aggregates have a height ranging around 20-25 nm and these structures are varying between 300-500 nm in width and up to 2 μ m in length.

In agreement with the literature data [18] specifying that small substituents on the 4-position of tetraaryl porphyrins favour π stacking, whereas those on 2 or 3 position prevent significant π stacking, and also in connection with our conclusions over UV-vis study, these aggregates are supposed to be co-facial assemblies.

4. Conclusions

New nanomaterials based on tetra-pyridylporphyrine entrapped in silica matrices were obtained by two steps acid-base catalysis sol-gel process and characterized by FT-IR, UV-vis, luminescence spectroscopy and AFM. The comparatively experiments were done by using two different acids in the first acid step catalysis, namely: HCl and glacial CH_3COOH . In order to optimize the immobilization process, a control of pH influence over accessibility of incorporation of porphyrin into silica was performed, certifying the generation of the dicationic specie and the significant aggregation processes of TPYP at pH values up to 4. UV-vis monitoring of the finally gelified materials and AFM imaging of the nanomaterial surfaces put into evidence that the aggregation of TPYP is due to π - π co-facial stacking. The intensity of the emission spectra of both nanomaterials is significantly increased in comparison with the silica matrix control sample, slightly higher when using HCl, proving that such materials, containing an organic photosensitizer, can be used in design of photocurrent generating hybrid devices in order to optimize light adsorption, surface binding, and charge transfer, with promising efficiencies in building of solar cells.

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