Nanostructured Glasses Based on Hybrid Silica Materials Incorporating a New Asymmetrical Phenyl-Substituted Porphyrin

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Abstract: The new asymmetrical, phenyl substituted porphyrin structure, namely: 5,10,15-tris(3-hydroxy-phenyl)-20-(3,4-dimethoxy-phenyl)-21H,23H-porphyrin, along with the nanostructured glasses and silica-based nanoparticles embedded with this compound were synthetized and characterized as to be designated for potential use in construction of advanced optoelectronic devices or electrochemical sensors. This porphyrin was synthesized by a multicomponent Adler-Longo type reaction using two different substituted aldehydes, and next characterized by HPLC, TLC, MS, UV-vis, fluorescence spectroscopy, AFM, ^{1}H-NMR and ^{13}C-NMR analysis. The observed changes in UV-vis and emission spectra were also discussed in terms of various pH conditions. The series of novel porphyrin-silica nanomaterials have been prepared by using silica matrices obtained in two variable sol-gel processes, *i.e. via* the one step acid- or two steps acid-base-catalyzed hydrolysis and condensation of tetraethylorthosilicate. Especially, the hybrid monolithic glass nanomaterials obtained here *via* the one step acid-sol-gel procedure exhibited a high intensity of the emission spectra bands and, besides, a very sharp bathochromic shift in the red region towards 723 nm, thus making also these nanoparticles as the valuable source of potential second generation photosensitizers. In the atomic force microscopy (AFM) measurements this hybrid nanomaterials displayed the spherical and highly monodispersed particles of ultra low size (less than 70 nm and with an average height of 20 nm), controlled shape, high porosity, and superior stability as the potential water-insoluble photosensitizers.

Keywords: Nanomaterials, tetrapyrrole macrocycles, silica matrix, spectroscopy, atomic force microscopy.

1. INTRODUCTION

A benefit brought by nanomaterials is their ability of varying their fundamental properties e.g. magnetization, optical properties, hardness, relative to bulk materials without a change in chemical composition, that enable the nanoporous materials to be used widely in mutual applications, such as luminescent materials [1], catalysts [2] versatile stationary phases in liquid chromatography [3], sensing of oxygen [4] or NO₂ at ppm levels [5], transducers in sensing systems [6] and so on. State of the art of nanomaterials research are based on techniques that afford the self-assembly of nanoscale species [7, 8] exhibiting a high surface areas and tunable, uniform pore sizes (2-10 nm) [9]. Furthermore, the most of hybrid materials obtained by

sol-gel process are usually non-toxic, inert, chemically and thermally stable, so they are widely applied where biocompatibility or thermal stability are required.

As the luminescence of porphyrin dopants in sol-gel glasses could be quenched by molecules and gases surrounding the glass, it is possible to design glasses that have optical properties which would be changed in the presence of target molecules, i.e. to make the sol-gel glass chemical sensors. Using the sol-gel process, it is possible to encapsulate the electrochemically active organic molecule in the pores of the glass in such way that these molecules are immobilized and cannot be leached out, while at the same time the glass is porous enough to allow the transportation of solvent and other small molecules or ions into the interior of the glass. Porous solids offer also the possibility of tailoring the properties of hybrids by the control of reactivity along pore walls through incorporation of different organic groups

The aim of the present work is to immobilize the newly synthesized compound 5,10,15-tris(3-hydroxy-phenyl)-20-(3,4-dimethoxy-phenyl)-21H,23H-porphyrin (THDMPP) into

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two different sol-gel matrices and obtaining in this way the new organic/inorganic hybrid nanomaterials belonging to Class I [10, 11] in which the organic phase is physically embedded inside the inorganic matrix thus providing enhanced luminescence, better sensitivity and improved stability. Because each molecule of mentioned THDMPP porphyrin is bearing three hydroxyl groups (Fig. **1**) it is possible that many stable hydrogen bonds to be formed between surface of silica particles and porphyrin guest. In this study, porphyrin-doped inorganic glasses of desired shapes and sizes were prepared by incorporating the THDMPP porphyrin-like dye in silica matrices obtained by the sol-gel process under acidic- or acid-base-condition, and intended for future potential application of such materials in construction of optical sensors of gases.

2. MATERIALS AND METHODOLOGY

2.1. Chemicals and Procedures

The 5,10,15-tris(3-hydroxy-phenyl)-20-(3,4-dimethoxy-phenyl)-21H,23H-porphyrin (THDMPP) was synthesized by a multicomponent reaction, as previously fully characterized and reported [12], with a major difference representing the molar ratio between 3,4-dimethoxybenzaldehyde : 3-hydroxybenzaldehyde : pyrrole, which was 1:3:4 in order to obtain better yields of the desired asymmetrical porphyrin. Reagents were *p.a.* grade and were purchased from Fluka, Aldrich and Merck and used as received, excepting pyrrole distilled prior to use. Thin-layer chromatography (TLC) was performed on 25 DC-Alufolien Aluminiumoxid 60 F254 Neutral (Merck). Solvent systems associated with R_f values and chromatography data are reported as v/v ratios. Column Chromatography was performed at room temperature on silica gel *60* (230 - 400 mesh, 0.040 - 0.063 mm), obtained from Merck.

Sol-Gel Preparations were done by adapting previously reported experimental data [13].

Synthesis of Control Silica Matrix by One Step Acid Catalyzed Sol-Gel Method: A mixture of H_2O (1.365 g, 0.076 mol, including the water from HCl solution) and HCl 37% (0.037 g, 0.38 mmol) were added by dripping under continuous stirring to a solution of TEOS (3.95 g, 0.019 mol) dissolved into EtOH (3.49 g, 0.076 mol). The molar ratios were: TEOS : EtOH : H_2O : HCl = 1: 4: 4: 0.02. The pH of the solution was 4.5. The reaction was performed for 30 minutes. After one week, the reaction mixture, kept at room temperature generated a transparent colorless stable gel.

Synthesis of Control Silica Matrix by Two Steps Acid/Base Catalyzed Sol-Gel Method: The first acid step catalysis sol-gel process was conducted by using the same reactants, ratios and conditions as reported above. After 15 minutes, the second basic step was started by slowly adding of NH_3 2.5%. A transparent gel was obtained instantly by using a total amount of 1.62 g solution of NH_3 2.5%.

Synthesis of Hybrid Porphyrin-Silica Nanomaterials: In each of the two used silica matrices, THDMPP (0.0011g, 0.015 mmol) dissolved into 5 mL THF were added by once to the broken freshly obtained gels. After 20 minutes of vigorous stirring of the fluidized gel, the gelation is finished, resulting an emerald green transparent gel in case of acid silica matrix and a violet transparent gel in case of acid-base

silica matrix. After drying 3 - 4 weeks at room temperature, dried gels are presenting as transparent light violet (acid-base catalyzed silica matrix) and emerald green (acid catalyzed silica matrix) strong glasses.

2.2. Apparatus and Measurements

UV-visible spectra were recorded on a UV/VIS PERKIN ELMER, LAMBDA 12 spectrometer. Fluorescence spectra were recorded in THF on a PERKIN ELMER Model LS 55 apparatus in a 1 cm cuvette. ^{1}H-NMR and ^{13}C-NMR spectra were registered on a 400 MHz and 100 MHz respectively BRUKER spectrometer, in $CDCl_3$. The chemical shifts are expressed in δ (ppm). The DEPT 135 experiments were done. Proton chemical shifts were internally referenced to the residual proton resonance in $CDCl_3$ (δ 7.26) and carbon chemical shifts were internally referenced to the deuterated solvent signals in $CDCl_3$ (the 3-line triplet signal around δ 77 ppm). The HPLC analysis were performed on a JASCO apparatus equipped with KROMASIL 100 SI 5μm polar column, 240 × 4 mm, i.d., with MD 1510 detector, at ambient temperature, using UV detection at 420 nm. The samples were subjected to analysis (20 μL) at a flow rate of 1 mL/min with acetone/hexane of ratio 1/1 as eluent. A 212 Varian Finnigan Mat mass spectrometer was used for registering MS. Pore size data (BJH method) were determined with QUANTACHROME Nova 1200 apparatus, by using nitrogen as adsorbate, at the temperature of liquid nitrogen 77.350K. The method for calculation was de Boer's (programme Quantachrome NovaWin2 - Data Acquisition and Reduction for NOVA instruments ©1994-2003, Quantachrome Instruments, version 2.1).

Surface Imaging: AFM measurements were performed in contact and tapping mode [9] with phase or frequency detection on a Model Innova SPM, made by Veeco; system software: SPMLab^{TM} v.7.0 for data acquisition and analysis were used. Atomic force microscopy (AFM) investigations were carried out also with a Nanosurf® EasyScan 2 Advanced Research AFM. Atomic force microscope measurements were made with sample preparation onto a silica plate. AFM data are quantitative on all three dimensions, the usual method for displaying them being by color mapping: in a gray scale, for example, dark and light tones represent the low, respectively high features. All AFM measurements were done in ambient conditions (temperature: 22 ± 2 °C; relative humidity: 50 – 70%)

Spectroscopic Studies: Absorption and fluorescence spectra were recorded at ambient temperature using 1 cm path length cells. All the fluorescence spectra were recorded with constant slit widths, 3 nm for excitation and 7 nm for emission. The pH values of the solutions were measured with a digital Radelkis pH-meter. The fluorescence quantum yield (ΦF) of porphyrin was calculated by using the steady-state comparative method [14-16].

3. RESULTS AND DISCUSSION

The analysis data certifying the structure of porphyrin THDMPP [12] are presented below:

5,10,15-tris(3-hydroxyphenyl)-20-(3,4-dimethoxyphenyl) porphyrin: violet cristals; yield: 8.6 %; mp over 320°C: ^{1}H-NMR (CDCl$_3$, 400MHz), δ, ppm: -2.79 (brs, 2H, NH), 2.64-2.68 (d, 3H, OH), 3.986(s, 3H, 3-OCH$_3$), 4.175(s, 3H, 4-

OCH₃), 7.07-7.22 (dd, 4H, *m*-Ph), 7.73-7.75 (d, 8H, *o*-Ph), 7.97 (brs, 3H, *p*-Ph), 8.64-8.89 (dd, 8H, β-Pyr typical for A₃B); ¹³C-NMR (CDCl₃, 100MHz), δ, ppm: 154.07, 149.29, 148.87, 147.05, 143.44, 134.68, 132.05, 131.07, 129.62, 127.86, 127.45, 121.89, 120.94, 118.27, 114.77, 109.42, 56.10; UV-vis, CHCl₃ (λmax (log ε): 421.75 (5.47); 518.11 (4.24); 554.46 (3.91); 591.90 (3.70); 649.22 (3.61); TLC (R$_f$ chloroform/dichloroethane/ethylic ether 5/5/1): 0.35; HPLC (R$_T$, min): 6.427; MS (54 eV):m/e= 722 M]$^{+\cdot}$ (C$_{46}$O$_5$N$_4$H$_{34}$]$^{+\cdot}$ molecular ion). Fluorescence quantum yield Φ$_f$=0.154.
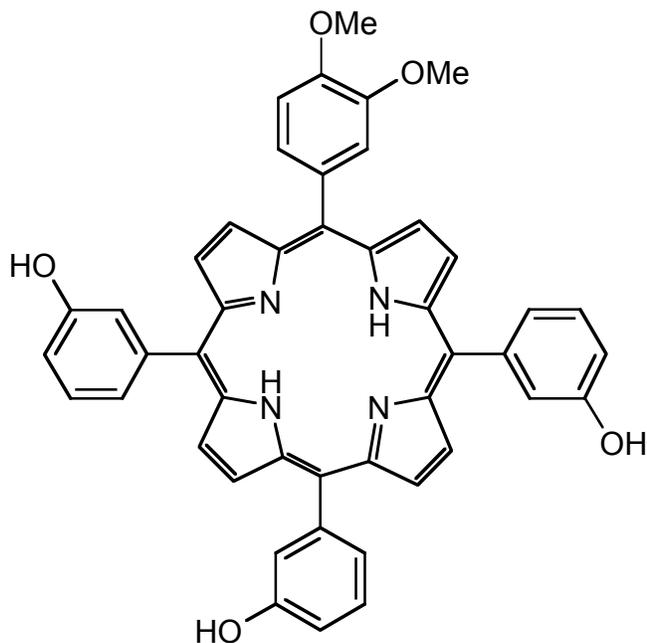
Fig. (1). Structure of 5,10,15-tris(3-hydroxyphenyl)-20-(3,4-dimethoxyphenyl)-21H,23H-porphyrin (THDMPP).

The UV-Visible spectrum in THF of the porphyrin THDMPP (Fig. **2**) is characterized by very intense Soret band at 418.93 nm (B band) and four Q bands of *etio* type allure, having smaller intensity, located at 515.33 nm Q$_{y(1,0)}$, 550.97 nm Q$_{y(0,0)}$, 593.09 nm Q$_{x(1,0)}$ and 650.43 nm Q$_{x(0,0)}$, respectively.

Strong acidic medium (pH = 2.5) produced Soret band splitting into two Lorentzian bands, situated at 421.19 and 459.12 nm respectively (Fig. **3**). The band centered on 421 nm is assigned to the monomer and the band located at 459 nm represent the self-assembly result of porphyrin to form J-type aggregates.

In strong acidic media, the QIV and QIII bands disappear while the QI grows in intensity and is red shifted towards 678.77 nm. Most of the free porphyrins in acid media manifest this behavior and the explanation is the higher symmetry of the porphyrin due to protonation and generation of the dication species. As already reported in the literature [17, 18] most of the porphyrins manifest a strong tendency to form aggregates in aqueous acidic solutions even at a concentration of 10^{-6} M, and also bind to acid-silica mainly in the form of aggregates, as illustrated in Fig. (**4**). The broad Soret and Q I bands in the UV-vis spectrum of the hybrid silica material, obtained by impregnation of porphyrin THDMPP into the silica matrix synthesized *via* one step acid sol-gel procedure, are both batochromic shifted, and supplementary, the QI band is manifesting an important hyperchromic effect.

The fluorescence quantum yield (Φ$_F$) of the porphyrin THDMPPP was evaluated in a solution of tetrahydrofuran and was calculated by the steady-state comparative method. The emission spectra of this porphyrin (Fig. **5**) exhibited two maxima, a strong and broad Q(0,0) fluorescence band near 655.56 nm, and a weaker emission band around 715 nm, assigned to Q(0,1) transition. The values of λem were obtained by exciting the samples at the wavelength of 550 nm.
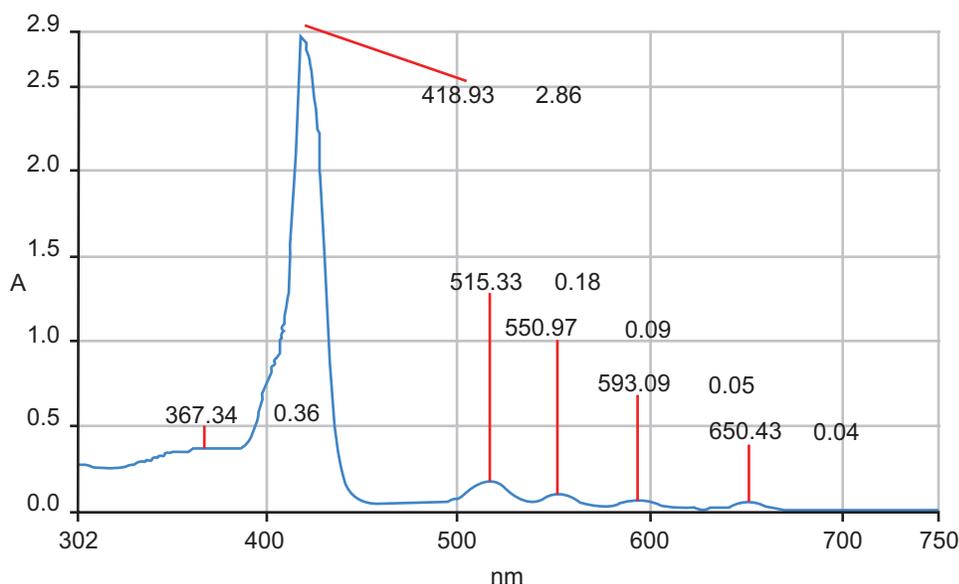
Fig. (2). The UV-vis spectrum of THDMPP in THF.
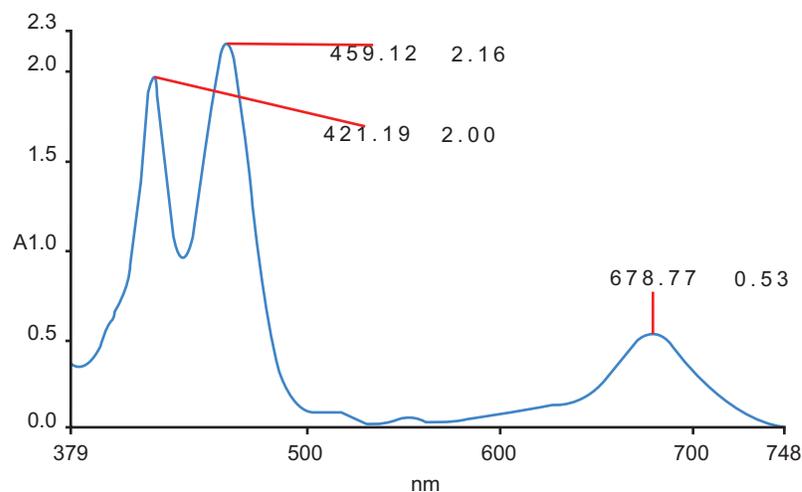
Fig. (3). The UV-vis spectra of THDMPP in THF-water system and acidic conditions (pH = 2.5).
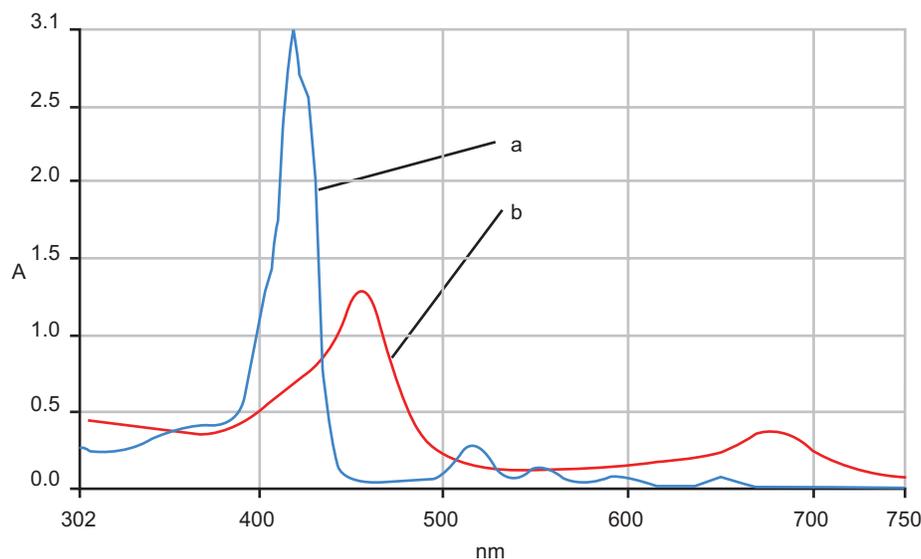
Fig. (4). The overlapped UV-vis spectra of free-porphyrin (line **a**), and of the hybrid silica material obtained by impregnation of porphyrin THDMPP into the silica matrix synthesized *via* one step acid sol-gel procedure (line **b**), in THF.

The original bands at 655 and 715 nm, observed in the fluorescence spectrum of the free porphyrin molecule in solution (Fig. **5**) are substituted by slight blue-shifted bands in the range 653-654 nm and a red shifted band in the range 715-719 nm in the emission spectra of the hybrid solid samples dissolved in THF (Fig. **6**). The most important fact regarding the emission spectra of hybrid porphyrin-silica materials, realized by impregnating silica matrix obtained by acid-catalyzed or by acid-base-catalyzed sol-gel process, is that the intensity of the main peak is remarkable increased in the hybrid materials comparatively with that of the free porphyrin. The intensity of the second peak, around 719 nm, is more than five times increased in the spectrum of impregnated silica matrix obtained by acid-catalyzed sol-gel process in comparison with that provided by free porphyrin, at the same concentration. After three month, when the gels are aged, it was observed that the red fluorescence

diminished or even disappeared, in accordance with literature data [19].

A red fluorescence shift was only noticed in the monolithic glass samples when the porphyrin, THDMPP was introduced into silica matrix synthesized *via* one step acid-catalyzed sol-gel procedure (Fig. **7**). The original band around 655 nm, observed in the fluorescence spectrum of the free-porphyrin in THF solution, is substituted by a blue-shifted band at 530.22 nm in the hybrid nanomaterial. On the other hand, the minor band became important and is red shifted to 723.47 nm. These transformations might be attributed to the surface environment around hybrid porphyrin-silica material and to the different polarity of the environment inside the pores of the gel.

By comparison, in case of hybrid nanomaterials obtained by impregnation of porphyrin THDMPP into the silica
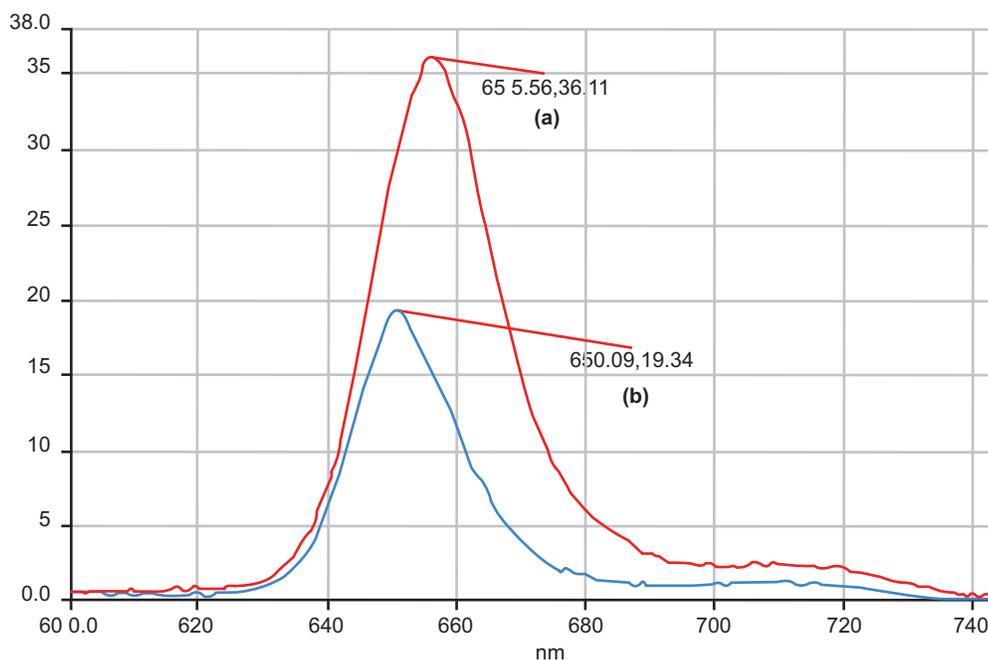
Fig. (5). Fluorescence emission spectra of the porphyrin (THDMPP) - line **a**, in comparison with TPP- line **b**, at the same concentration, 1.11×10^{-6} M, in THF. The spectra were measured with the excitation of 550 nm.
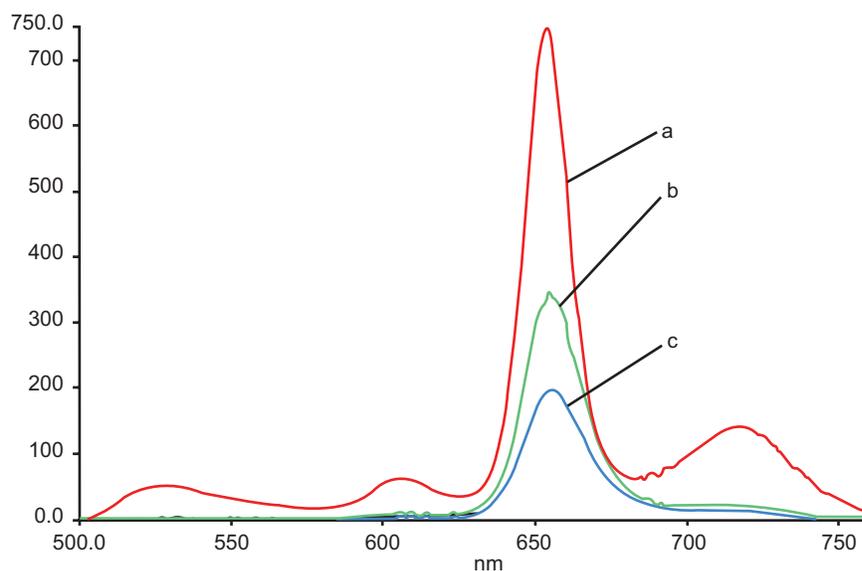
Fig. (6). Superposed emission spectra of hybrid nanomaterials obtained by impregnation of porphyrin THDMPP into the silica matrix synthesized: *via* one step acid sol-gel procedure (line **a**); *via* two steps acid-base sol-gel procedure (line **b**) and of free porphyrin (line **c**), in THF, at the same concentration $c = 4.0 \times 10^{-5}$M.

matrix synthesized *via* two steps acid-base sol-gel procedure, there is to be noticed only a slight decrease of the intensity of the emission bands with aging (Fig. **7**, line b).

In order to study silica nanomaterials textural properties nitrogen adsorption desorption analysis at 77 K has been performed. Specific surface area (S_{BET}), pore volume (V_p) and pore size distribution (D_p) as well as properties of intrapore surface of mesoporous materials are presented in Table **1**. These analyses were performed for both of the hybrids and the control silica-gels samples. In case of silica

obtained with acidic catalysts, transparent gels of low porosity are obtained, whereas with basic catalysts transparent gels of high porosity are made [20, 21] Porphyrin entrapping into the gel determined, in each case, a decrease of the surface area than in the case of control samples. The explanation might be that the porphyrin is trapped inside of the silica network.

The AFM measurements reveal important data regarding the topography of the surface, shape, morphology and dimension of THDMPP porphyrin aggregates impregnated in
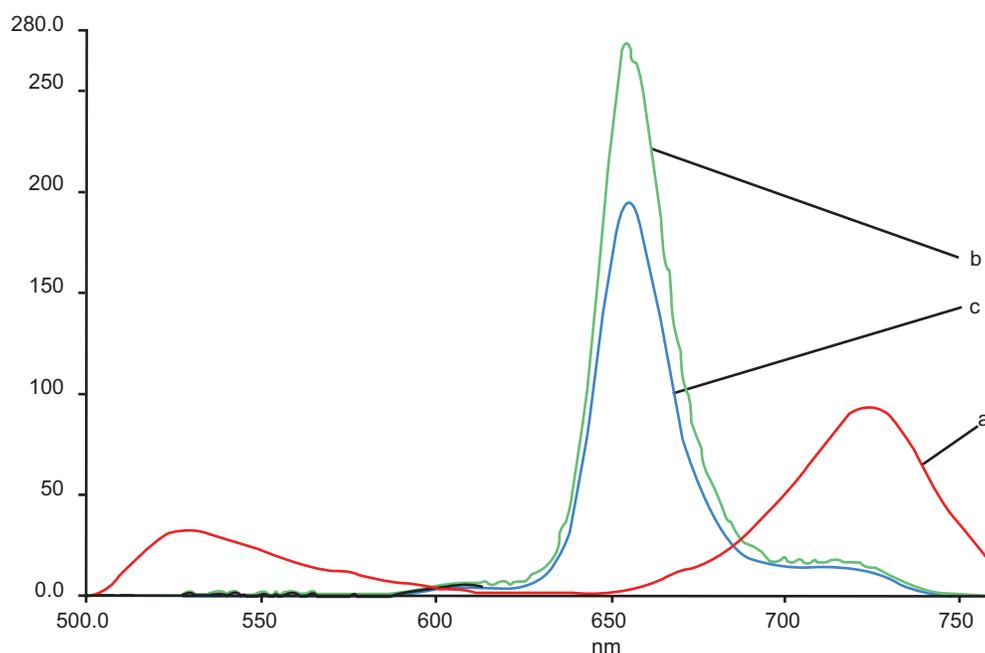
Fig. (7). Superposed emission spectra of hybrid nanomaterials obtained by impregnation of porphyrin THDMPP into the silica matrix synthesized: *via* one step acid sol-gel procedure (line **a**); *via* two steps acid-base sol-gel procedure (line **b**) and of free porphyrin (line **c**), in THF, at the same concentration $c = 4.0 \times 10^{-5}$M, after the gels are aged in time of three months.

silica matrices. AFM images of porphyrin-base (Fig. **8**) on pure silica plates reveal structures with 70 - 400 nm size, which presumably corresponds to the porphyrin aggregates on the silica surface. The heights of the aggregates are varying between 0.2 - 4.2 nm with maximum height of 20 nm. The heights of pores are of maximum 6 nm. The distance between two aggregates is in the range of 30 to 164 nm. Atomic force microscopy particle analysis of the hybrid nanomaterials obtained by impregnation of porphyrin THDMPP into the silica matrix synthesized *via* one step acid sol-gel procedure (Fig. **9**), revealed on the material surface 929 grains of 35 - 73 nm in diameter with an average height of 20 nm, a volume of 0.005 μm^3 for a single grain and an area of 0.31 μm^2.

Measurements data obtained by atomic force microscopy analysis of the hybrid nanomaterials obtained by impregnation of porphyrin THDMPP into the silica matrix synthesized *via* two steps acid-base catalysis sol-gel procedure (Fig. **10**) revealed relative uniform aggregates with dimensions both in length and in width in the range of 63 - 75 nm. The topography of the surface of the hybrid silica-porphyrin nanomaterials depends on the flexibility of the porphyrin core that allows for a conformational
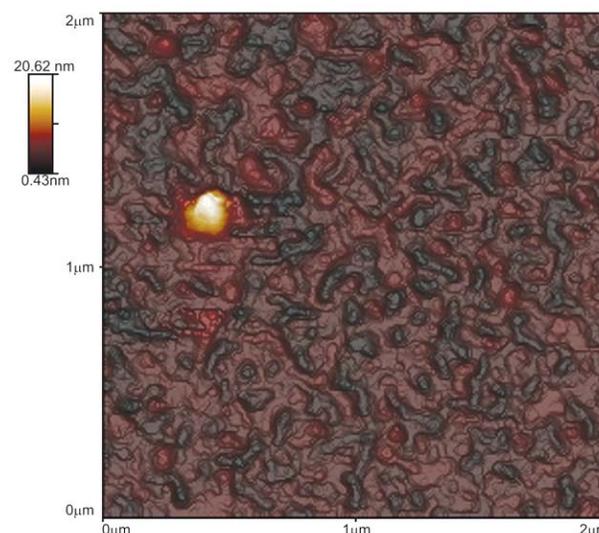
Fig. (8). Tapping mode atomic force microscopy of pure porphyrin (THDMPP) deposited on pure silica plates (2μm × 2μm). The samples were formed by solvent evaporation from a THF solution containing the compound.

Table 1. BET Analysis Data of THDMPP-Silica Hybrid Materials

Sample	Pore Size Diameter D_p [ads] (nm)	Pore Size Diameter D_p [des] (nm)	Surface Area S_{BET} (m²/g)	Pore Volume V_p (mL/g)
Hybrid THDMPP-silica acid catalyzed	1.38	1.78	326.6	0.139
Control silica acid catalyzed	1.95	2.23	532.65	0.301
Hybrid THDMPP - silica acid-base catalyzed	1.82	2.60	465.05	0.162
Control-silica acid-base catalyzed	3.40	3.81	1074.54	0.792

the porphyrin-like dye in silica matrices obtained by the sol-gel process under acidic or acid-base condition. The organic/inorganic hybrids belong to Class I nanomaterials. Providing enhanced red luminescence and tunable pore sizes diameter of 1.3-3.8 nm, these hybrid nanomaterials might be used in formulation of the sol-gel glass chemical sensors.

(a)

(a)

(b)

(b)
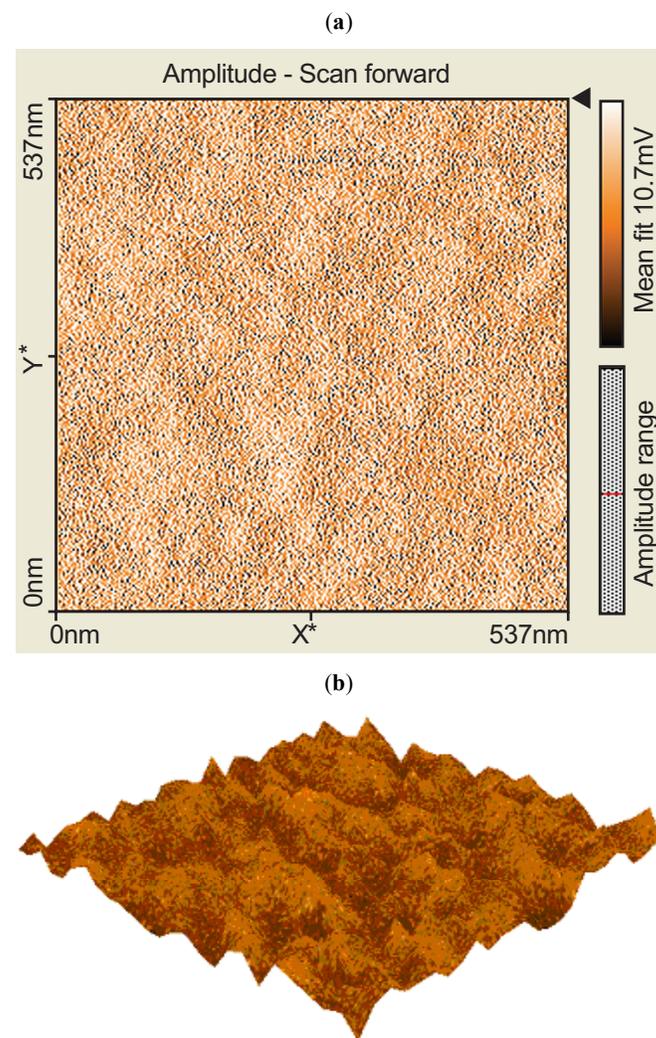
Fig. (10). 2D (**a**) and 3D (**b**) AFM image (537 × 537 nm) of the surface of nanomaterials obtained by impregnation of porphyrin THDMPP into the silica matrix synthesized *via* two steps acid-base catalysis sol-gel procedure (software: NanoSurf EasyScan2).

Fig. (9). AFM image (2 × 2μm) (**a**) and particle analysis from a section (20 × 20μm) (**b**) of the hybrid material obtained by impregnation of porphyrin (THDMPP) into silica matrix derived from one step acid sol-gel process.

adaptation of the molecule to the local environment of the pores [22] and also is suffering much influence on the type of catalysis of sol-gel method performed for the obtaining of silica matrices. These materials do not have high ordered range of nanoporous structure, with distinct orientation or packing of the nanopores, but they have tunable pore sizes diameter of 1.3 - 3.8 nm.

4. CONCLUSIONS

In this study, 5,10,15-tris(3-hydroxy-phenyl)-20-(3,4-dimethoxy-phenyl)-21H,23H-porphyrin-doped inorganic glasses of desired shapes and sizes were prepared by incorporating

ABBREVIATIONS

AFM   = Atomic force microscopy

TEOS   = Tetraethylorthosilicate

THDMPP = 5,10,15-Tris(3-hydroxy-phenyl)-20-(3,4-dimethoxy-phenyl)-21H,23H-porphyrin

THF   = Tetrahydrofurane

TLC   = Thin-layer chromatograph

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