Advanced silica-matrix material entrapping a hydroxy-substituted porphyrin compound. Synthesis and characterization

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A new inorganic-organic hybrid material consisting in porphyrin, namely: 5,10,15,20-tetrakis(4-hydroxyphenyl)-21H,23H-porphine, encapsulated in silica matrix is obtained. A few preliminary tests, which have been done in order to optimize the immobilization process, using different sol-gel techniques: *in situ*, by impregnation and by sonication, are presented. Porphyrin molecules are introduced into silica gels without major changes regarding their photoactivity, but with a side reaction due to porphyrin aggregation, and significant hyperchromic effects regarding Q bands. The compositions were characterized by using spectroscopic methods such as FT-IR and UV-vis.

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1. Introduction

The present study is dealing with the obtaining of advanced transparent hybrid silica materials encapsulating 5,10,15,20-tetrakis(4-hydroxyphenyl)-21H,23H-porphine**, (TOHPP)**. They have been prepared successfully via the two steps acido-basic catalyzed hydrolysis and condensation of tetraethylorthosilicate using different approaches of the sol-gel process: *in situ*, by impregnation and by sonication. The synthetic conditions have been studied.

The sol-gel process involves two steps [1]. In the first step, silicon alkoxides are hydrolyzed by mixing with water and either an acid or a base can serve as catalyst. The second step involves a lot of types of polycondensation reaction, as represented in equations (1-3).

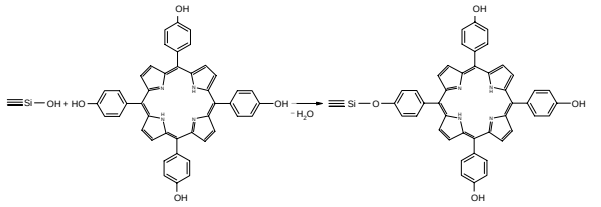
The obtained compositions were characterized by using FT-IR and UV-vis, spectroscopic methods.

$$\equiv Si—OR + H_2O \longrightarrow \equiv Si—OH + ROH \quad (1)$$

where $R = C_2H_5$

$$\equiv Si—OH + \equiv Si—OR_1 \longrightarrow \equiv Si—O—Si\equiv + R_1OH \quad (2)$$

where $R_1 = H, C_2H_5$



(3)

2. Experimental

Reagents: Tetraethyl orthosilicate (TEOS, 98%, Fluka), tetrahydrofuran (THF, 98%, Merck), ethanol absolute (EtOH, Chemopar) were all used without further purification. TOHPP was synthesized by Adler method using reported procedures [2].

Apparatus: FT-IR spectra were registered on a JASCO 430 FT-IR apparatus as KBr pellets. UV-visible spectra were recorded on a UV/VIS PERKIN ELMER, LAMBDA 12 spectrometer. An Ultrasonic Cole Parmer Cleaning Bath, working at 56 KHz frequency, was used.

***In situ* two steps acid/base catalyzed sol-gel method starting fromTEOS.** A mixture of H_2O and HCl 37% were added by slow dropping under vigorous stirring to a solution of TEOS dissolved into EtOH. The following molar ratios were kept constant during the first acidic step: TEOS: EtOH: H_2O: HCl=1: 4: 4: 0.02. After 15 minutes, the second basic step was started by slowly adding of NH_3 2.5%. At the moment when viscosity has been increased, a 7.85 mM solution of TOHPP in THF was added by once (molar ratio: TEOS: TOHPP=1:0.05). The basic catalysis was controlled by continuous slowly adding of NH_3 2.5%.

The final material was a transparent red stable gel. After the wet gel was dried for 8 hours at 100 °C, the color turned into green. The etalon sample was identically synthesized, without porphyrin adding and a transparent gel was obtained.

Porphyrin entrapping by impregnation within a silica matrix derived from a two steps acid/base sol-gel process, by using TEOS as precursor. The first acid step catalysis was done identically with *in situ* method. The second basic step was started by slowly adding of NH_3 2.5% until a transparent gel was obtained. An identical amount of solution consisting in TOHPP in THF was added by once to the gel, which was firstly smashed and than vigorously stirred. After 15 minutes of stirring, the gelation is finished (red transparent gel).

***In situ* sol-gel method using TEOS by sonication** was conducted in acido- basic catalysis by porphyrin impregnation, in identical previously described conditions. During the sonication (110 minutes), the temperature increased from 25 °C to 48 °C. The porphyrin-sol-gel hybrid material was gelified after 24 hours, resulting in a red transparent gel.

3. Results and discussion

The chemical structure of hybrid materials, of TOHPP and etalon samples are characterized by FT-IR spectroscopy and exemplified, (Fig. 1), for *in situ* sol-gel method using TEOS in acido- basic catalysis. All the FT-IR spectra of the hybrid materials have the same allure. The FT-IR spectrum of TOHPP presents the main absorption bands of strong intensity located at 3415 cm^{-1}, assigned to O-H stretching vibration and the absorptions at 3317 and 967 cm^{-1} which are attributed to stretching and bending vibrations of N-H and C-N, respectively.

Both spectra of silica-etalon sample and porphyrin-silica material exhibit a broad band between 3100 and 3700 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 difference between these two spectra can be noticed within the 1300 - 1000 cm^{-1} region. In a similar manner with reported data [3] the bonding mode from 1090 to 1150cm^{-1} is assigned to the Si-O-Si asymmetric stretching mode and symmetric stretching was at 723 cm^{-1}, which were due to the formation of silica structure via sol-gel process with TEOS [4]. Absorption peaks of Si-O-C at 625 and 852 cm^{-1} were also found.

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.

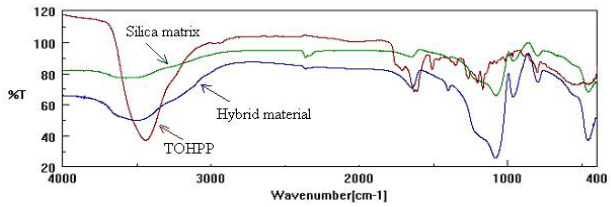


Fig. 1. FT-IR of superposed TOHPP, hybrid material and silica matrix etalon sample. In situ sol-gel method, using TEOS in acido- basic catalysis.

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 TOHPP bending-groups were not clearly identifiable because they overlap with the broad bands of Si-O-Si and Si-O-C in hybrid material [5]. This supplementary feature [6] could indicate that silica component was covalently bonded to the organic TOHPP.

The two steps acid-base catalyzed sol-gel process has been monitored by UV-vis spectroscopy. As expected, the spectrum of the silica etalon sample without porphyrin possessed no absorption bands in the UV-vis range. Spectrum of the TOHPP in THF is an *etio* type spectrum (Fig. 2), with a typical Soret band, which arose from transition of $a_{1u}(\pi)$ - $e_g^*(\pi)$, and the four Q-bands in the visible region corresponding to $a_{2u}(\pi)$ - $e_g^*(\pi)$ transitions.

UV-vis Spectrum of the hybrid material registered after acid first step catalysis possesses only three absorption bands at 451, 561 and 677 nm (Fig. 3) and the color of the reaction mixture is green. The first band, assigned to the Soret region, is strongly bathochromic shifted with 32 nm in comparison with the Soret band in porphyrin free-base spectrum.

The last band belongs to the Q region exhibiting both bathochromic and hyperchromic effects. In the present case, in acidic medium, QI band is bathochromic shifted with 27 nm, being more intense than that of porphyrin free base (log ε = 4.45 in comparison with log ε = 3.25 in TOHPP). This behavior can be a result of protonation of the free base. The explanation for the higher intensity of Q I band than Q II band in the spectra of the hybrid material, is that, under light exposure in acidic medium, porphyrin transforms into chlorine or even bacteriochlorine [7].

Further adding of base compound (2.5% NH_3) turned the color of the reaction mixture in yellowish-green and the UV-vis spectrum of the second sample was shown in Fig. 4. The observed Soret band is splitted into two signals demonstrating that an association of porphyrin molecules has occurred. As in Fig. 3 the QI band is more increased in intensity as it was expected. At a certain moment of basic catalysis step, the change in color from green to red occurs. This spectrum is similar to the spectrum of free TOHPP excepting that all the absorption bands, especially Q bands, exhibit a hyperchromic effect when TOHPP is encapsulated in silica matrix (Fig. 5).

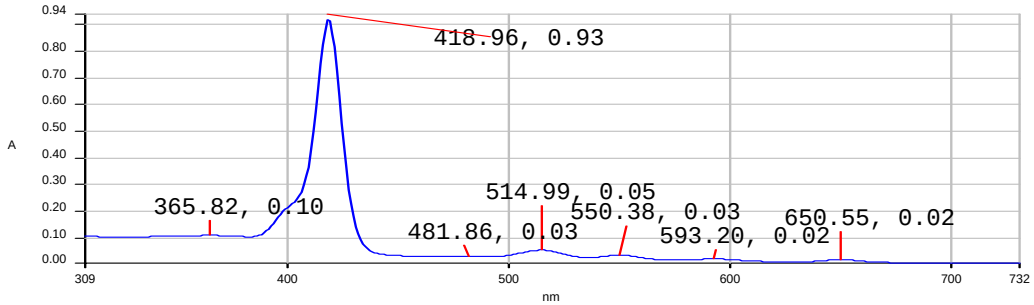


Fig. 2. UV-vis Spectrum of the porphyrin free-base in tetrahydrofuran λ max(log ε): 418.96 (4.92); 514.99(3.65); 550.38(3.43); 593.20(3.25); 650.55(3.25).

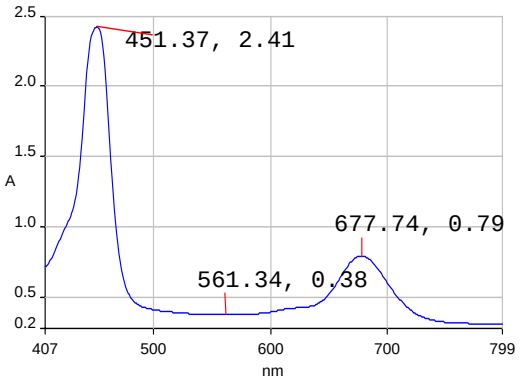


Fig. 3. UV-vis Spectrum of sol-gel sample with protonated porphyrin (green color) λ max(log ε): 451.37 (4.99); 561.34(4.19); 677.74(4.45).

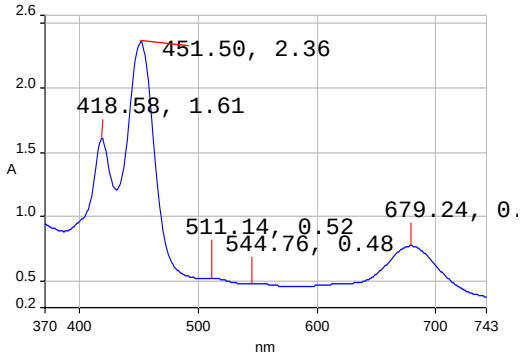


Fig. 4. UV-vis Spectrum of green sol-gel sample in the early stage of base step catalysis λ max(log ε): 418.58 (4.81); 451.50(4.98); 511.14(4.33); 544.76(4.29); 679.24(4.50).

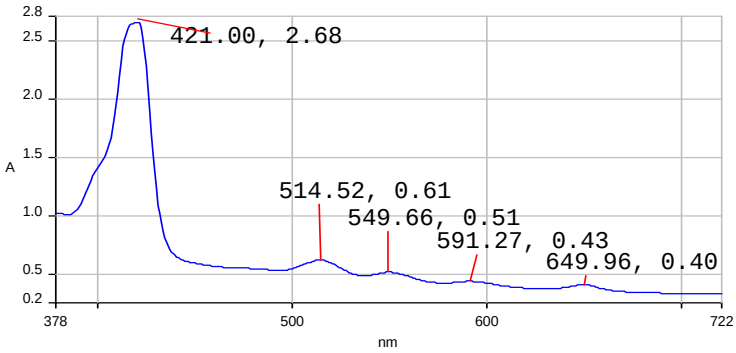


Fig. 5. UV-vis Spectrum of sol-gel sample when color turned from green to red (regenerated porphyrin) λ max(log ε): 421.00 (5.04); 514.52(4.40); 549.66(4.32); 591.27(4.24); 649.96(4.21)

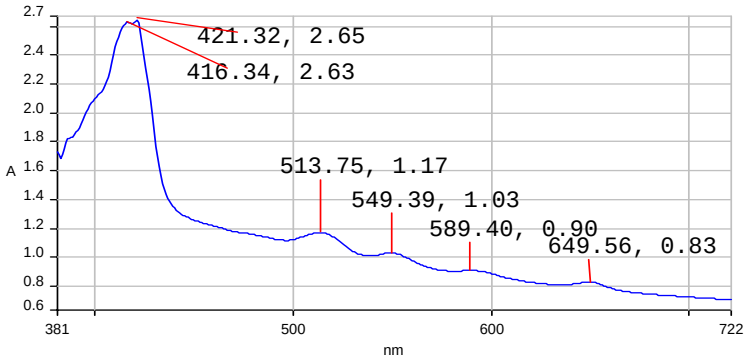


Fig. 6. UV-vis Spectrum of sol-gel sample at the gelation point λ max(log ε): 421.32 (5.03); 416.34(5.03); 513.75(4.68); 549.39(4.62); 589.40(4.56); 649.56(4.53)].

It can be clearly seen that finally the porphyrin molecules are introduced into silica gels without major changes regarding their photoactivity, but with a process of porphyrin aggregation (Fig. 6). The slight splitting of the Soret band points out that the dye molecules tend to aggregate also by π–π and hydrophobic interactions [8].

The photoactivity is finally increased (>120%) in the range of Q bands (500-650 nm) of porphyrin-silica matrix sample (log ε>4.5) in comparison with Q bands of the free-base porphyrin (log ε<3.65).

4. Conclusions

New inorganic-organic hybrid materials, (Class II, [9]), consisting in 5,10,15,20-tetrakis(4-hydroxy-phenyl)-21H,23H-porphine encapsulated in silica matrix have been prepared.

UV-vis study put into evidence that during the sol- gel process of polycondensation, major changes regarding porphyrin ring structure occur, most probable because of the protonation of free base during acid step catalysis. Porphyrin molecules are finally introduced into silica gels without major changes regarding their structure and photoactivity, but with porphyrin aggregation and hyperchromic effects regarding Q bands. FT-IR spectra demonstrated that in all cases the silica component is covalently bonded to the organic porphyrine.

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