Spectroscopic characterization of water-soluble cationic porphyrins in sol–gel silica matrices and coatings

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Abstract

Silica aerogels doped with different concentrations of water-soluble cationic porphyrins were synthesised by the sol–gel polymerisation of tetraethylorthosilicate (TEOS). Porphyrin dimer formation in sol–gel matrices was studied in the function of gelation time, over the porphyrin concentration range up to 10^{-5} M. The deviation from the linearity of Beer–Lambert law starts with porphyrin concentration about 5×10^{-6} M. The dimerization constants were estimated. The similar dependence could be observed for the aerogels and the solid thin films. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Water-soluble cationic porphyrins; Sol–gel matrices; Sol–gel coatings; Dimerization; Dimerization constants

1. Introduction

The possibility of mixing organic and inorganic compounds in a new unique hybrid material is realized by sol–gel method. The entrapment of organic reagents into sol–gel matrices and coatings has been the objective of much research since Avnir and co-workers pointed out the role of such systems for sensing purposes [1]. Sol–gel monoliths and sol–gel thin films are very useful to

encapsulate various guests such as inorganic clusters [2–4], lanthanide complexes [5,6], laser dyes [7,8] and bioactive molecules [9,10]. Porphyrins and their metal complexes are very fascinating class of dye molecules whose functions vary from oxygen and electron transport (hemoglobin, cytochrome c) to solar energy transfer (chlorophyll) in photosynthesis. The sol–gel immobilization of porphyrins in suitable matrices has been reported in literature due to the importance of these systems from many points of interest, such as: chemical and biochemical sensing [11–14], optical limiting [15–17], hole-burning [18,19] and catalysis [20].

Many cationic and anionic porphyrins are known to dimerize and to further agglomerate in

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aqueous solutions. Hetero- and selfassociation of porphyrins have attracted considerable attention, as they play important role in biochemistry and photochemistry [21–23]. Recently the process of the cationic porphyrin dimerization turned out to be significant in the binding of cationic porphyrins to DNA [24,25]. The study of the dimer formation of organic dopants in sol–gel materials has received relatively little attention, despite the fact that monomer–dimer equilibria determine optical and photochemical behavior of the organic dyes. Only dimerization of the rare earth and copper phthalocyanines in sol–gel glasses [5,26] and rhodamine B in dip-coatings have been reported [27–29].

We present our study on the encapsulation of two water-soluble cationic porphyrins: tetrakis[4-(trimethylammonio)phenyl] ($H_2TTMePP$, Scheme 1) and tetrakis (1-methyl-4-pyridyl) ($H_2TMePyP$, Scheme 2) in the monolith aerogels and solid thin films obtained by sol–gel method. We also report the details of the absorption spectra of these porphyrins in monolith matrices and in dip-coated thin films. The aerogels samples with different concentrations of the porphyrins were prepared by tetraethoxysilane (TEOS) hydrolysis. Deviation from the linearity of the Beer–Lambert law, as a function of gelation time was used to study the dimerization as an initial step of porphyrin agglomeration in silica aerogels.

Scheme 1. $H_2TTMePP$ -5,10,15,20-Tetrakis[4-(trimethyl-ammonio)phenyl]-21 H ,23 H -porphine, tetra- p -tosylate salt.

Scheme 2. $H_2TMePyP$ -5,10,15,20-Tetrakis(1-methyl-4-pyridyl)-21 H ,23 H -porphine, tetra- p -tosylate salt.

2. Materials and methods

2.1. Synthesis of silica alcogels

The alcogels with various amounts of $H_2TMePyP$ or $H_2TTMePP$ were synthesized by the sol–gel polymerization of tetraethyl orthosilicate [$Si(OC_2H_5)_4$ –TEOS]. HCl was used as a hydrolysis catalyst and NH_3 aq. as a condensation catalyst to synthesise TEOS alcogels. We mixed 10 cm³ of TEOS (Aldrich, research grade) with 1 cm³ of formamide (Aldrich, research grade) and added distilled water and HCl (Zakłady Azotowe Tarnów-Moscice S.A.). Formamide was added in order to obtain crack-free monoliths. After hydrolysis, we added NH_3 aq. (P.O.Ch. Gliwice) to the TEOS mixture. Mixture was doped with water solutions of $H_2TMePyP$ and $H_2TTMePP$ to achieve appropriate concentration of porphyrin in alcogel. Then, the sol was gelled in disposal polyacrylic cells sealed with parafilm to measure light absorption after gelation. Later parafilm was perforated to allow evaporate pore solvent during monolith drying. The following mole ratio was used: [TEOS]:[H_2O]:[formamide] = 2:11:1. Gelation was finished within 1 h after 120 min of hydrolysis. Absorption spectra of porphyrins in alcogels were collected just after gelation and later during ageing of alcogels.

2.2. Preparation of silica aerogels

The alcogels synthesized according to the above procedure have the structure filled with water. Wet gels were dried in the desiccator over water at temperature of 40 °C for 3–4 weeks up to the moment when dimensions of the shrinking monoliths were constant. The changes in absorption spectra of porphyrins in gels were controlled during time of drying.

2.3. Preparation of silica coatings

Coatings were prepared by dipping onto glass slides. Sols were prepared starting from TEOS prehydrolyzed with concentrated HCl in ethyl alcohol medium. The following mole ratio was used: [TEOS]:[H₂O]:[C₂H₅OH] = 1:4:8. Porphyrin was added to the mixture in the form of powder, whereas it dissolved quickly. Sols were stirred for 1 h at room temperature. A dipcoating technique described by Villegas and Pascual [30], was used to obtain thin coating upon common soda-lime glass slides. Coatings were dried at 60 °C for 3 days.

2.4. Measurements

Absorption spectra of porphyrins in water solutions, alcogels, and coatings were measured with a Carl Zeiss-Jena M42 spectrophotometer in the 300–900 nm region at a temperature of 21 ± 1 °C. Spectra were stored on disk under control of Carl Zeiss program WASPECT. The database program SIGMAPLOT was used for manipulation and plotting of the spectra.

3. Results and discussion

Absorption spectra of H₂TTMePP and H₂TMePyP in different media are illustrated in Figs. 1 and 2. In both cases two main bands were found in the region of 400–450 nm and 500–650 nm which are known as the porphyrin Soret and *Q* band, corresponding to absorption transition of $S_0 \rightarrow S_2$ and $S_0 \rightarrow S_1$, respectively. The Soret band arises from allowed electronic transitions

and is about 15 times more intensive than *Q* band which occurs as a result of forbidden electronic transitions. Comparing the aerogel porphyrins spectra to these in water solution we can say that the overall characteristics are similar. However some changes in peak intensity and wavelengths are observed. The molar extinction coefficients (ϵ) shown in Figs. 1 and 2 were found experimentally for the water solutions of porphyrins. For the monoliths and thin films ϵ were determined from absorbance values, taking thickness of the samples into consideration. The intensity of the Soret band in sol–gel material is insignificantly lower than in water solution. The Soret bands are red shifted and a broadening of these bands occurred. In addition, molar extinction coefficient is lower in aerogel than in water. The four *Q*-bands undergo changes that are more complex. The

Fig. 1. Absorption spectra of the H₂TTMePP in: water solution (solid line), monolithic sol–gel material (dotted line) and thin film (dash line); ϵ = molecular extinction coefficient.

Fig. 2. Absorption spectra of the $H_2TMePyP$ in: water solution (solid line), monolithic sol–gel material (dotted line) and thin film (dash line); ϵ = molecular extinction coefficient.

bands $Q_{y(1,0)}$ and $Q_{y(0,1)}$ are blue shifted while bands $Q_{x(1,0)}$ and $Q_{x(0,1)}$ are red shifted. These results were interpreted as arising from the less polar silica matrix, which consisted of Si–O–Si and Si–O groups what was observed for the octaethyl porphyrin in the earlier report [11].

The spectra of $H_2TTMePP$ and $H_2TMePyP$ in silica coatings (Figs. 1 and 2—dash lines) differ from these ones in aerogel and water. The porphyrins undergo the following protonation equilibria:

At room temperature and acidic conditions the central nitrogen atoms of the N_4 porphyrin moiety are protonated in two steps according to the Eqs. (1) and (2). In the spectrum of $H_2TTMePP$, sol–gel silica thin coating on soda lime slides (Fig. 1—dash line), two Soret subbands can be observed. The main component of this band is shifted seriously (from 419 to 439 nm). The Soret band of $H_2TMePyP$ is also dramatically shifted from 423 to 435 nm (Fig. 2). For both porphyrin Q bands only two instead of four bands can be observed. Such spectral changes suggest that on the acidic soda-lime glass porphyrins exist in protonated form of dication H_4P^{2+} . This suggests that dip-coatings containing cationic water-soluble porphyrin can be used as pH sensors operating in different region of pH for different porphyrins.

The absorbance spectra of porphyrins were recorded periodically while alcogel samples were dried, that is when process of the aerogel formation from alcogel has occurred. The spectra of aerogels doped with $H_2TTMePP$ increasing concentration are shown in Fig. 3. Spectra were recorded during shrinking sol–gel monolith, and later absorbance was normalised to the 10 mm path length to observe the deviation from the Beer–Lambert's law. Fig. 4 shows the parallel set of spectra for the $H_2TMePyP$ porphyrin, but as the starting gel had thickness of 3 mm and later it shrunk upon drying, the thickness of aged gel was every time measured and absorbance was normalised to 3 mm path length. When we compare spectra of porphyrin just after gelation with the spectra after 19 days of drying, only increase in band intensities can be observed. This is due to increase of porphyrin concentration when water is evaporated and pores of gels are closed.

An example of the Soret band absorbance changes with concentration of the porphyrin in sol–gel monolithic glasses during drying is shown in Fig. 5. Series of such plots were used to estimate the porphyrin dimerization constants in silica matrices. It is known that Soret band of porphyrin is extremely sensitive to dimerization and that free-base porphyrin in water solutions are in monomer form in a concentration range of 10^{-5} mol dm $^{-3}$ [31–33]. With the assumption that in aged aerogel pores only monomers and

dimers occur, the following equilibrium between monomer and dimer can be written:

$$K_D = \frac{[(\text{H}_2\text{P})_2]}{[\text{H}_2\text{P}]^2} \quad (6)$$

where K_D is dimerization constant in mol dm^{-3} . On this base, following the classical work of Pasternack et al. [34] the Eq. (7) can be derived.

$$A = \frac{\varepsilon_d C_0}{2} + \frac{(2\varepsilon_M - \varepsilon_D)(\sqrt{8K_D C_0 + 1} - 1)}{8K_D} \quad (7)$$

where C_0 is the total concentration of porphyrin; A is the measured absorbance of porphyrin at Soret band; ε_M and ε_D are the molar coefficients of extinction of monomer and dimer. This equation

Fig. 3. Absorption spectra of the H_2TMePP in 10 mm monolithic sol–gel material as a function of porphyrin concentration before drying (a) and after 19 days of drying.

Fig. 4. Absorption spectra of the H_2TMePyP in 3 mm monolithic sol–gel material as a function of porphyrin concentration before drying (a) and after 19 days of drying.

connecting equilibrium constant of the reaction with changes in absorbance was used in order to calculate dimerization constant based on Lambert–Beer's experiment. For the calculation of dimerization constants, the experimental data were fitted to Eq. (7) using the non-linear fitting procedure based on the Marquardt–Levenberg algorithm (program Sigma Plot—Jandel Corp.). For the fitting the water solutions molar coefficients of extinction were used. However these coefficients are changed during gels drying, we can neglect it, inasmuch results of the fitting are very similar, even if ε_M is considered as an approximate parameter. An example of the fitting is shown in Fig. 5 where experimental points are in

Fig. 5. Plot of the absorbance at the Soret band of $H_2TMePyP$ vs. C_M of porphyrin in function of drying time. Symbols are experimental points; the theoretical curves are generated from Eq. (7).

good agreement with the theoretical curve generated from the Eq. (7). The estimated values of the dimerization constants are presented in Table 1. The range of the dimerization constants is the same to that known from the literature for water solution [35,36]. Values of the dimerization constants from Table 1 are insignificantly decreasing along with the time of monolith samples drying. During the sol–gel glasses drying, the amount of the solvent in the pores is decreasing. These are conditions that favour the dimerization process but, on the other hand, with the progress of drying, dimerization could be gradually prevented by the steric hinderance of the forming SiO_2 network and monomer porphyrin becomes preferable

Table 1
Influence of the monolithic sol–gel glasses drying time on the values of porphyrin dimerization constants K_D (M^{-1})

Time of drying (days)	$H_2TMePyP$	$H_2TTMePP$
0	$3.6 \times 10^5 \pm 180$	$6.8 \times 10^5 \pm 380$
4	$2.6 \times 10^5 \pm 260$	$5.7 \times 10^5 \pm 540$
6	$1.4 \times 10^5 \pm 210$	$5.8 \times 10^5 \pm 750$
9	$1.3 \times 10^5 \pm 620$	$4.2 \times 10^5 \pm 230$
19	$1.0 \times 10^5 \pm 340$	$2.9 \times 10^5 \pm 870$

form. The slight decrease of the K_D upon drying can be also explained by the change of ionic strength of dried silica gels.

4. Conclusions

(1) Absorption spectra of cationic water-soluble porphyrins in solutions and sol–gel matrices indicate only small differences. Only insignificant changes in molar coefficients of extinction and wavelength are observed.

(2) Porphyrin dimer formation in sol–gel matrices was studied in the function of gelation time. The deviation from the linearity of Beer–Lambert law starts with porphyrin concentration about 5×10^{-6} M. The dimerization constants slightly decreasing along with the time of monolith samples drying what can be explained by gradual preventing of dimerization by steric hinderance of the forming SiO_2 network and by the change of ionic strength of dried silica gels.

(3) The dimerization constants for the ammonio porphyrin ($H_2TTMePP$) are during gel drying always higher than for the methyl-pyridyl porphyrin ($H_2TMePyP$), due to more spatial groups $-N(CH_3)_3^+$ which give stronger interaction than methyl-pyridyl groups.

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