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Spectroscopic studies on the inclusion complexes of tetrakis(2-hydroxy-5-nitrophenyl)porphyrin with a-cyclodextrin in solution and in sol–gel matrix[*]

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Tetrakis(2-hydroxy-5-nitrophenyl)porphyrin included in α-cyclodextrin (α-CD) photophysics was studied in aqueous media, in solid state and entrapped in a sol–gel matrix. The equilibrium constant of the pair porphyrin/α-CD was evaluated as $1.22\cdot10^5$ $\mathrm{mol^{-1}\cdot dm^{-3}}$. The nitroporphyrin was reduced to aminoporphyrin, included into the α-CD and then entrapped in the Si–O matrix network. The tetrakisporphyrin maintained its luminescent properties (with emission bands at 658 and 713 nm, excited at 422 nm) in all environments, indicating a structural stability under the experimental conditions.

Key words: *tetrakis(2-hydroxy-5-nitrophenyl)porphyrin, aminoporphyrin, a-cyclodextrin, sol–gel, luminescence, inclusion compound, hybrid matrix*

1. Introduction

The central importance of porphyrins in heme proteins has stimulated much interest in their water-soluble derivative model compounds. Porphyrins are investigated and employed in a wide range of fields such as catalysts of oxidation processes, biomimetic compounds, supramolecular devices, in design for new products in medicine and as contrast agents for magnetic resonance imaging [1–4]. Cyclodextrins (CD) are cyclic oligosacharides composed of 6, 7 and 8 glucose units, named α-, β- and γ-CD, respectively [5–6]. Cyclodextrins are moderately soluble in water and are known to include molecules or fragments in their hydrophobic cavities. This inclusion may perturb the photophysical and photochemical properties of the encapsulated guest molecule [7, 8].

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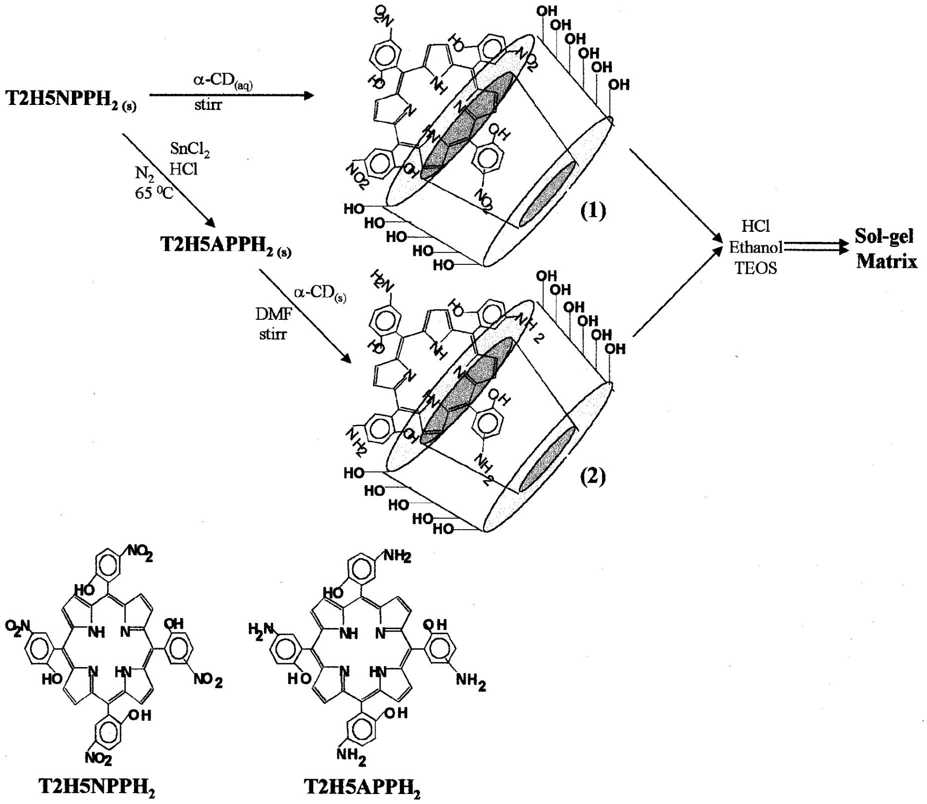
Scheme 1



Scheme 1. Preparation route of $T2H5NPPH_2$ (**1**) and $T2H5APPH_2$ (**2**) α-CD inclusion compounds entrapped in sol–gel matrix

Sol–gel materials popularity results from a number of interesting features, including that they can be manufactured at low temperatures; their microstructure can be controlled to some extent; they are optically transparent and have some other promising properties [9]. The most current methodology consists in the hydrolysis of an alkoxide precursor followed by condensation and polymerization to produce a gel with a continuous inorganic network [10, 11].

In this work we studied the inclusion complex of tetrakis(2-hydroxy-5-nitrophenyl)porphyrin ($T2H5NPPH_2$) with α-cyclodextrin **(1,** Scheme 1**)** in aqueous solution and in a solid state. The solid inclusion compound was studied when it is doped in a rigid sol–gel matrix. Similarly, we also investigated the tetrakis(2-hydroxy-5-aminophenyl)porphyrin ($T2H5APPH_2$), which we expected to be covalently linked to the α-cyclodextrin **(2,** Scheme 1**)**.

2. Experimental procedure

α-cyclodextrin and TEOS (tetraethylorthosilicate) were purchased from Aldrich. $T2H5NPPH_2$ was synthesized as described in [12] and transformed to $T2H5APPH_2$ by reduction with $SnCl_2$ and HCl, under nitrogen atmosphere, at 65 °C (FTIR = 1658 cm^{-1}, $n NH_2$) [13]. To obtain the inclusion complex **(1)**, a solution of $T2H5NPPH_2$ in dichloroethane (DCE) was added to a α-cyclodextrin aqueous solution (1:100 molar ratio). The two-phase system were stirred and heated (~40 °C) until all DCE was evaporated and the porphyrin transferred to the aqueous solution. To determine the equilibrium constant (K_1) between the porphyrin and α-CD, 5.0 cm^3 of a $3.5\cdot10^{-5}$ $mol\cdot dm^{-3}$ solution of $T2H5NPPH_2$ in DCE was added into equal volume of α-cyclodextrin aqueous solution at various concentrations (4.9; 3.5; 1.75; 1.05; 0.7; 0.35($\times10^{-5}$) $mol\cdot dm^{-3}$). After the porphyrin addition, the by UV-Vis absorption spectra were recorded. The solution with a molar ratio 1:100 ($T2H5NPPH_2$:α-CD) was evaporated and the solid complex was analyzed by excitation and emission luminescence spectroscopy.

In order to prepare solid matrices, 2.0 cm^3 of ethanol, 2.0 cm^3 of TEOS, 1.0 cm^3 of water and 0,750 cm^3 of HCl (1.0 $mol\cdot dm^{-3}$) was added into 10.0 mg of $T2H5NPPH_2$-α-CD and $T2H5APPH_2$-α-CD complexes, respectively. The resulting solution was stirred for 30 minutes and then allowed to stand at 25 °C. A xerogel with glassy appearance was obtained after 3 days of aging for both complexes. The materials were submitted to absorption in infrared region and luminescence analyses. The absorption spectra (UV-Vis) were recorded on an UV-Vis spectrophotometer (Hewlett Packard 8452 Diode Array). FTIR spectra were recorded for solid materials in KBr pellets, in a Perkin Elmer FT-IR 1600. The luminescence data were obtained in a spectrofluorometer (SPEX Fluorolog III TRIAX550) at room temperature. The fitting curve was obtained by using the ORIGIN® program.

3. Results and discussion

The synthetic route for preparation of the inclusion complexes is shown in Fig. 1. To form inclusion complex, $T2H5NPPH_2$ in DCE was stirred with α-CD in aqueous solution. The equilibrium constant (K_1) was estimated for the formation of 1:1 inclusion complex from the equation [14]:

$$\frac{1}{(A-A_0)}=\frac{1}{a'}+\frac{1}{a'K_1[a-CD]} \tag{1}$$

where a' is a constant. The equation is valid only if the concentration of porphyrin is much lower than the concentration of α-CD.

The absorption UV-Vis spectra of the $T2H5NPPH_2$-α-CD solutions (maxima at 432 nm), with increasing α-CD concentration, are shown in Fig. 1. The plot of $1/(A–A_0)$

against 1/[α-CD] gives a straight line (Fig. 2), and, from this plot ($Y = A + BX$, where $A = 3.88539$, $B = 3.19345\cdot10^{-5}$) we evaluate that the K_1 value is $1.22\cdot10^{5}$ $\text{mol}^{-1}\cdot\text{dm}^{-3}$. Moreover, this plot suggests the formation of the 1:1 T2H5NPPH$_2$-α-CD inclusion complex:

$$\alpha\text{-CD} + \text{T2H5NPPH}_2 \overset{K_1}{\leftrightarrows} \alpha\text{-CD}\cdot\text{T2H5NPPH}_2$$

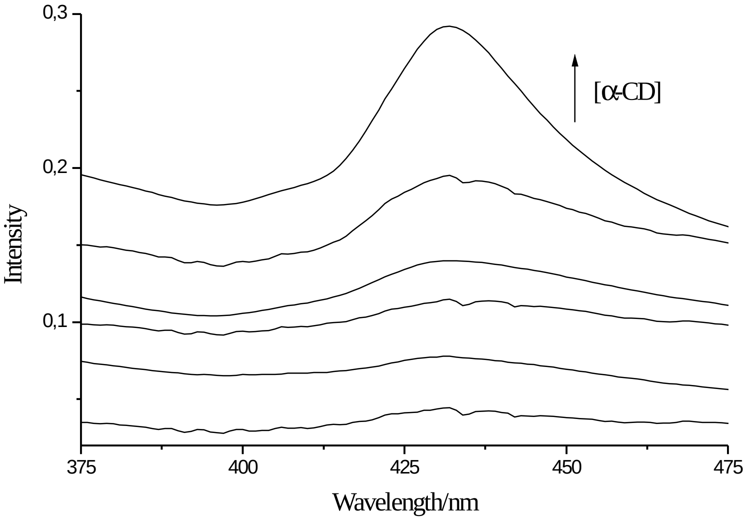


Fig. 1. Absorption spectra of T2H5NPPH$_2$ ($3.5\cdot10^{-5}$ mol·dm^{-3}) in aqueous solutions of the following concentrations of α-CD: $0.35\cdot10^{-5}$; $0.7\cdot10^{-5}$; $1.05\cdot10^{-5}$; $1.75\cdot10^{-5}$; $3.5\cdot10^{-5}$ and $4.9\cdot10^{-5}$ mol·dm^{-3}

For the inclusion of water-soluble tetrakis(4-sulfonatophenyl)porphyrin in α-CD, Hamai and Koshyama [15] obtained the value of $7.2\cdot10^{2}$ dm^{3}·mol^{-1} for the 1:1 inclusion complex. Also Mosinger et al. [16] found the value of $4.5\cdot10^{3}$ mol^{-1}·dm^{-3} as the equilibrium constant for same anionic porphyrin into 2-hydroxypropyl α-CD. This higher value for K_1 is consistent with our results, since we observed that the uncharged porphyrin formed a more stable system with the hydrophobic pocket of the CD.

The emission spectra of T2H5NPPH$_2$ in DCE, T2H5NPPH$_2$-α-CD inclusion complex (in aqueous solution and in a solid state) and the sol–gel matrix are shown in Fig. 3. The peaks related with these spectra are presented in Table 1. The excitation (at approximately 422 nm) and emission bands (at 658 and 713 nm) are the same in all environments, indicating that the T2H5NPPH$_2$ maintained its luminescent properties and structural stability under the experimental conditions.

FTIR spectroscopy of the T2H5NPPH$_2$-α-CD in sol–gel matrix was undertaken to confirm the formation of the Si–O bond (Table 1). The IR spectrum showed a band at 1073 cm^{-1} correspondent to a Si–O stretching mode [17], indicating the formation of the matrix network.

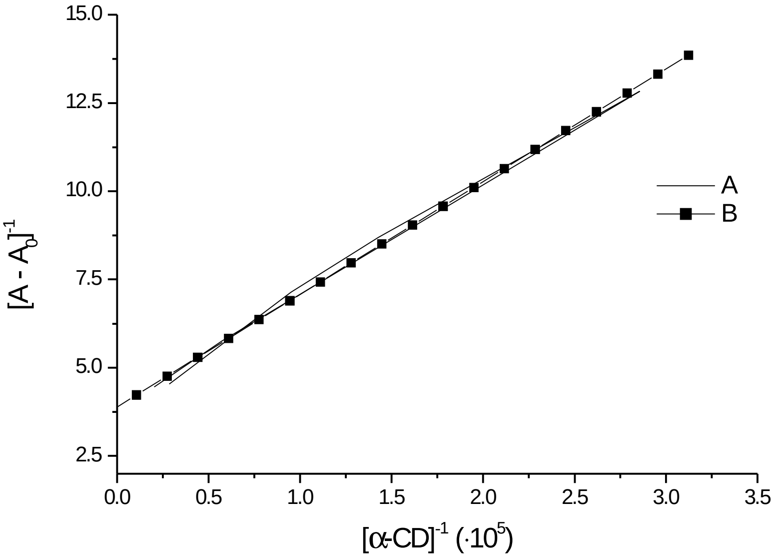


Fig. 2. Doubly-reciprocal plot for the absorbance of T2H5NPPH$_2$ (3.5·10^{-5} mol·dm^{-3}) in aqueous solution containing various amounts of α-CD (λ_{obs} = 432 nm) (A) and the fitted linear equation $Y = A + B$; A = 3.88539 and B = 3.19345·10^{-5}

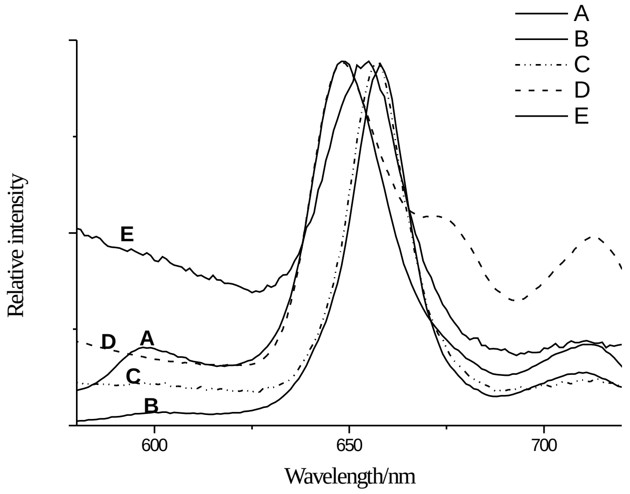


Fig. 3. Emission spectra: T2H5NPPH$_2$ in DCE (A), T2H5NPPH$_2$ with α-CD inclusion compound in water (B) and in a solid state (C); T2H5NPPH$_2$ (D) and T2H5APPH$_2$ (E) with α-CD inclusion compound in sol–gel matrix

The luminescence spectra of T2H5APPH$_2$-α-CD showed the maximum peak of excitation at 426 nm and of emission at 648 nm (Fig. 3), similar to the correspondent T2H5NPPH$_2$. The FTIR spectrum of the T2H5APPH$_2$-α-CD did not confirm the formation of a secondary amine bond, what points to the formation of the inclusion complex between α-cyclodextrin and tetrakis(2-hydroxy-5-aminophenyl) [T2H5APPH$_2$-α-CD (**2**)], that is not covalently bonded. The FTIR band at 1658 cm^{-1} (νNH$_2$ of T2H5APPH$_2$), 1158 cm^{-1} (group C–O–C of CD) and 3373 cm^{-1} (group C–OH of CD) confirmed that the structures of porphyrin and cyclodextrin are not modified in the sol–gel process.

Table 1. Excitation and emission maximum and FTIR assignments obtained for T2H5NPPH$_2$ and T2H5APPH$_2$ and their inclusion compounds with α-CD in different media

Compound	Excitation l_{max}/nm	Emission l_{max}/nm	FTIR [11] n/cm^{-1}	assignment
α-CD solid	–	–	1154 3400	C–O– C C–OH
T2H5NPPH$_2$ in DCE	422	658, 713	–	–
T2H5NPPH$_2$-α-CD (aq)	427	657, 713 (w*)	–	–
T2H5NPPH$_2$-α-CD (s)	425	654, 713 (w)	1582 3403	–NO$_2$ C–OH
T2H5NPPH$_2$-α-CD sol–gel matrix	424	598, 648, 713	1073	Si–O
T2H5APPH$_2$-α-CD sol–gel matrix	426	648, 713	1658 1080	–NH$_2$ Si–O

*w – weak.

4. Conclusions

T2H5NPPH$_2$ maintained its luminescent properties in all environments: aqueous media, solid state and in sol–gel matrix, suggesting a structural stability under the experimental conditions. In addition, an enhancement in the emission of T2H5NPPH$_2$-α-CD in the inorganic matrix has been observed, leading to the conclusion that the use of α-CD is a valid methodology to solubilize organic molecules in order to produce designed luminescent materials by the sol–gel technology.

Acknowledgements

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