

Luminescent Hybrid Porphyrinosilica Obtained by Sol Gel Chemistry

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The sol-gel process is a methodology used to obtain organic-inorganic hybrid solids, which open new possibilities in the field of material science. The sol-gel technique offers a low temperature attractive approach for introducing organic molecules into amorphous materials. In order to introduce tetrakis (2-hydroxy-5-nitrophenyl)porphyrin covalently bounded to a silicate matrix, the inorganic precursor 3-isocyanatopropyltriethoxysilane was added (molar ratio 2:1) to the porphyrin solution in anhydrous dimethylformamide and triethylamine. The isolated porphyrin and the hybrid porphyrinosilica have excitation maximum centred at 400 nm and 424 nm, respectively and the emission spectra for both materials has bands centred at 650 nm and 713 nm. The formation of hybrid matrix was investigated by FTIR.

Keywords: *hydroxyporphyrin, nitroporphyrin, sol-gel, hybrid material, and luminescence*

1. Introduction

Hybrid materials, in which organic molecules are incorporated into a silica matrix using the sol-gel process¹, have properties of an inorganic matrix and the functionality of the organic component. Using the sol-gel methodology at temperatures < 100 °C materials with higher purity and homogeneity can be obtained¹. Modified orthosilicates can be used to link organic monomers to the matrix producing new materials with a variety of shapes, including thin films and monoliths². These materials have attracted interest due to the possibility of combining the properties of organic compounds with the thermal properties of inorganic oxides³⁻⁴.

The development of sol-gel derived hybrids where luminescent centers are incorporated in organic or inorganic hosts is a recently theme in the field of luminescent materials^{5,6}. These materials combine the absorption of ultraviolet light and subsequent highly efficient emission⁷. Incorporation of chromophores such as porphyrins or metalloporphyrins into polymer networks has been investigated for applications in catalysis and sensor devices.

These materials have required optical quality and mechanical strength⁸. Their optical transmission in visible range is good and they can be polished. Such materials with emission, absorption, second-order nonlinear and photochromic properties have been used in photonic devices⁹. The porphyrin appended polymers belong to the class of luminescent polymers. These luminescent polymers play an important role in the fields of photovoltaics, electroluminescence, light emitting diodes and lasers and are actively studied¹⁰⁻¹².

Sol-Gel method has been proposed¹³ to create solid-state visible laser for medical applications, such as photodynamic therapy (PDT), which is an approach for treatment of malignant tumors, and laser-induced fluorescence (LIF) diagnostics. Both techniques need lasers emitting in the red region of the spectrum. Today the most common clinically used photosensitizers are porphyrin structurally related with absorption peaks at 405 and 650 nm. The latter peak is used for the PDT since the living tissue has a good light transmission at this wavelength⁵. This work presents the synthesis of a new red luminescent hybrid porphyrinosilica, which we label T2H5APPH₂ incorporated into a silicate matrix, by sol gel methods and data on its properties.

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2. Experimental

Materials

Triethylamine, 3-isocyanatopropyltriethoxysilane-IPTES and tetraethoxysilane- TEOS were purchased from Aldrich. The precursor tetrakis (2-hydroxy-5-nitrophenyl) porphyrin - T2H5NPPH₂ was synthesized in our laboratory by the Adler Longo Method¹⁴.

Instruments

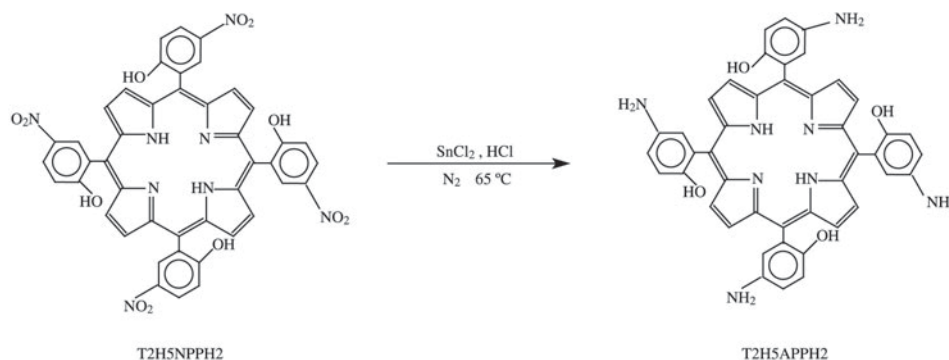
The absorption spectra were recorded in an UV/Vis spectrophotometer (Hewlett Packard 8452 Diode Array), luminescence data in a spectrofluorometer (SPEX Fluorolog Triax III) at 25 °C and FTIR spectra in a Perkin Elmer FTIR 1600.

Preparation of the tetrakis(2-hydroxy-5-aminophenyl) porphyrin - T2H5APPH₂

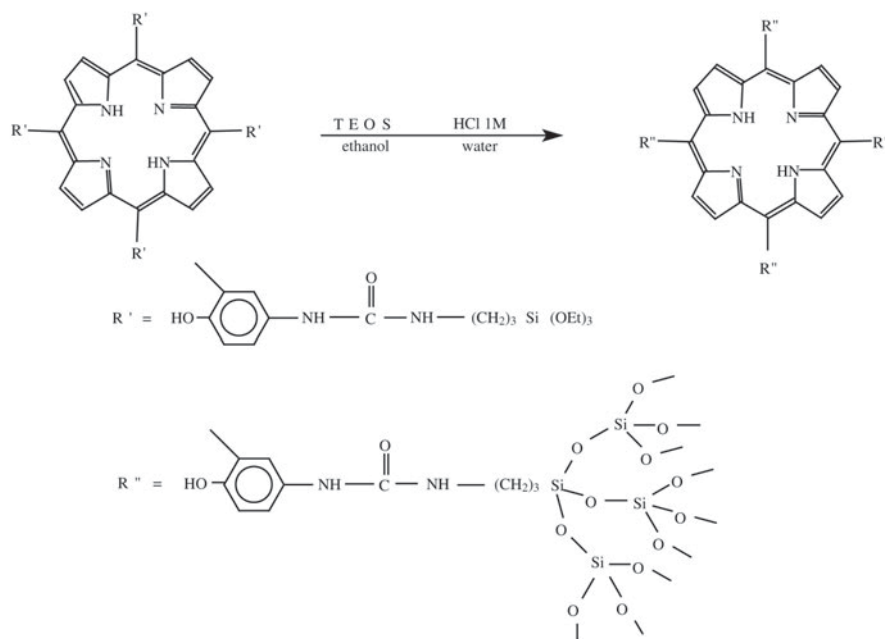
T2H5NPPH₂ (5.9×10^{-5} mol) was dissolved in concentrated HCl (8 ml), water (12 ml) and SnCl₂·2H₂O (17.9×10^{-5} mol) was added. The solution was stirred at 65 °C for 1h, in N₂. After cooling in an ice bath, the mixture was neutralized with NH₄OH 2 mol/l until a pH 7.5 was obtained. The solvent was eliminated on a rotatory evaporator. The T2H5APPH₂ was extracted from the solid by successive addition of ethanol and UV/Vis and FTIR measurements made.

Preparation of the urea silyl porphyrin monomer precursor

The preparation was followed the scheme 2: IPTES (2.4×10^{-5} mol) was added to a solution of T2H5APPH₂



Scheme 1. Synthesis of T2H5APPH₂.



Scheme 2. Synthesis of the T2H5APPSG.

(4.8×10^{-6} mol) and triethylamine (2.4×10^{-5} mol) in anhydrous dimethylformamide (4 ml). The resulting mixture was stirred, and refluxed for 8 h. UV/Vis and FTIR spectrometers measured the attained monomer.

Preparation and characterisation of the porphyrinosilica - T2H5APPSG

To 1.00 ml of DMF solution monomer, we added 2.00 ml of ethanol, 2.00 ml of TEOS, 720 ml of water and 250 ml of HCl 1M. The resulting mixture was stirred for 30 minutes and stand in an opened vial at 25 °C for solvent evaporation and gelation process occurs. In 2 days the mixture became viscous and in 5-10 days a xerogel with glassy appearance was obtained. The final product T2H5APPSG, porphyrinosilica, was ground and washed with acetone e ethanol and measured by UV/Vis, Luminescence and FTIR spectrometers.

3. Results and Discussion

The UV-Vis absorption spectra of the reduced porphyrin T2H5APP₂ is shown in Fig. 2 (I_{\max} : 418 Soret, 514 and 650 nm in ethanol). The characteristic^{8,15} nNH₂ was observed in the FTIR spectra at 1629 cm⁻¹.

The silyl porphyrin monomer precursor (Fig. 1) was prepared through the reaction of amino groups present in the porphyrin with the isocyanate group present in the IPTES. The amount of monomer formed was verified through the determination of the concentration of the porphyrin that did

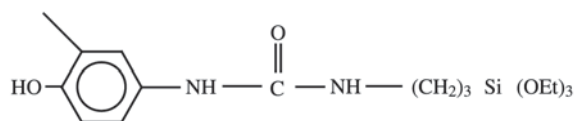


Figure 1. Structure of the Monomer.

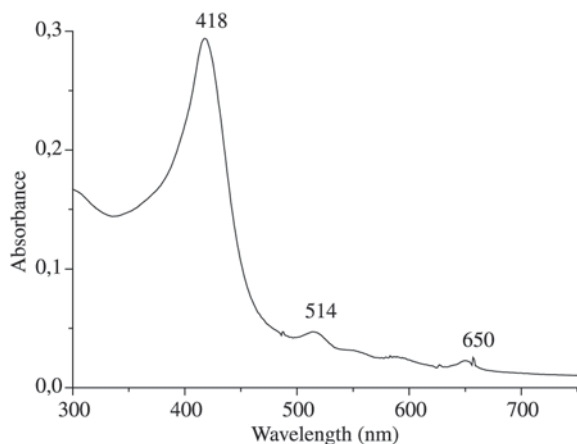


Figure 2. Absorption spectra of T2H5APP₂ in ethanol.

not react with IPTES. The spectrum at the solid was measured in the UV-Vis (ethanol), I_{\max} : 420 (Soret) and 550 nm. The FTIR (KBr) present the characteristic frequencies at 1654 cm⁻¹ relative to the carbonyl group (nC = O) and 1086 cm⁻¹ relative to the siloxanes (nSi-O)^{8,15}.

The porphyrinosilica samples were characterized through the measurements of ctra UV/Vis absorption spectra, luminescence and FTIR spectra. UV/Vis absorption spectra, Fig. 3, shows the absorption spectra of T2H5APPSG solid. The spectrum of the T2H5APPSG shows that the functionalization of the porphyrin does not modify the characteristic Soret band of monomer and the T2H5APP₂. UV-Vis (solid), I_{\max} : 420 nm (Soret) and 550 nm⁵.

The emission spectrum (I_{exc} : 424 nm) of the solid T2H5APPSG, Fig. 4, has bands at 650 nm and 713 nm (the same as the porphyrin). As in the absorption spectra, the similarity of the emission spectra means that the luminescent properties of the porphyrin were retained after the hybrid preparation⁸.

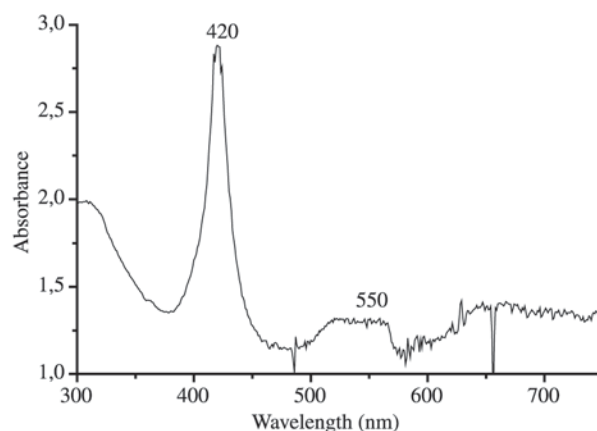


Figure 3. Absorption spectra of T2H5APPSG solid.

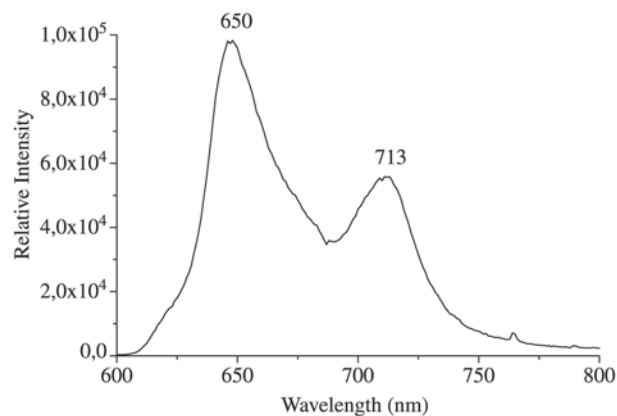


Figure 4. Emission spectrum of T2H5APPSG solid.

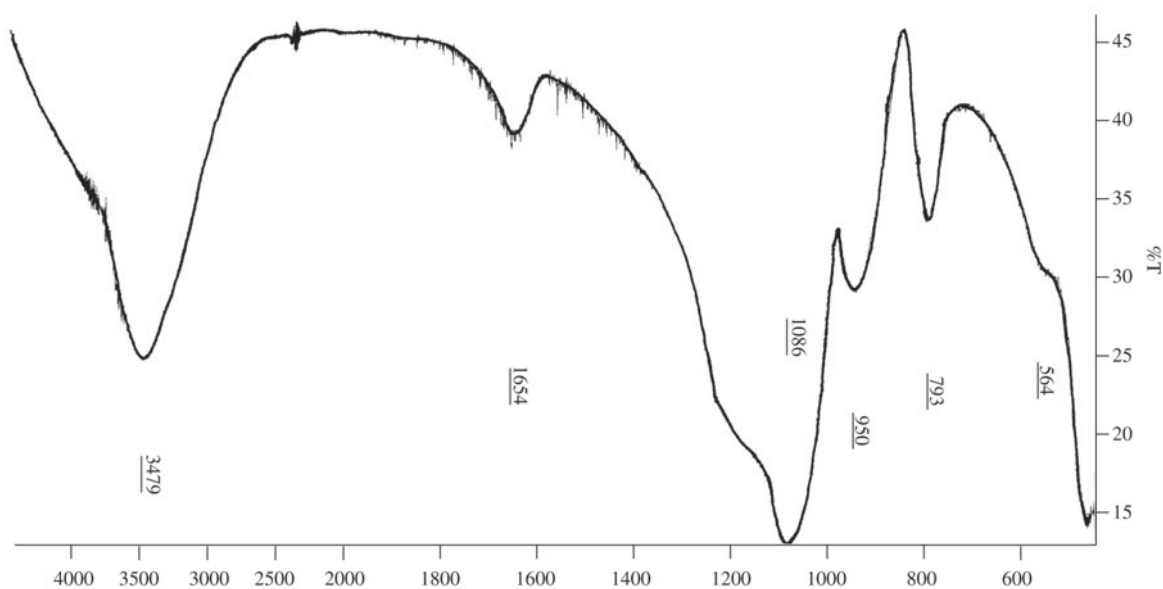


Figure 5. FTIR spectrum of T2H5APPSG solid in KBr.

Table 1. Bands of the FTIR spectrum of T2H5APPSG solid in KBr.

n (cm ⁻¹)	IR Assignment
3479	OH (porphyrin)
1654	C=O (carbonyl group)
1086	Si-O (Siloxane)
950	C=C (aromatics)
793	C=C (aromatics)
564	C=O (amide)

The FTIR spectrum of the solid T2H5APPSG, Table 1 and Fig. 5, shows bands at 1654 cm⁻¹ relative to the carbonyl group (nC=O) and 1086 cm⁻¹ relative to the siloxanes (nSi-O)^{8,15}. These assignments would indicate if the functionalization occur.

4. Conclusion

As we demonstrated, the sol-gel process has been proved to be a valid methodology to produce a stable, designed luminescent porphyrin-based hybrid material, which can be shaped for the applications in the fields of photovoltaics, electroluminescence, light emitting diodes and lasers, as mentioned in the literature (10-12).

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