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Fluorescent tetraruthenated porphyrins embedded in monolithic SiO_2 gels by the sol–gel process

Shirleny F. Santos [a], Marcelo L. Santos [a], Luis E. Almeida [a], Nivan B. Costa Jr. [a], Iara F. Gimenez [a], Koiti Araki [b], Ildemar Mayer [b], Fabio Monaro Engelmann [b], Henrique Eisi Toma [b], Ledjane S. Barreto [a,*]

[a] Departamento de Química—UFS, CEP 49100-000, São Cristóvão, SE, Brazil
[b] Instituto de Química—USP, CP 26.077, CEP 05599-970, São Paulo, SP, Brazil

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Abstract

In this work silica gels have been prepared by a sol–gel method using tetraethylorthosilicate as gel precursor. The tetraruthenated porphyrins H_2(3-TRPyP), Co(3-TRPyP), and H_2(4-TRPyP) were incorporated into the systems during gel formation without problems commonly found in the process, such as aggregation. Spectroscopic studies of the resulting silica gels revealed the presence of absorption bands in the range 200–400 nm associated with the transitions of the groups ruthenium–bipyridine, along with the Soret band at the same wavelengths observed in solution. The porphyrins were found to preserve fluorescence emission properties in the range 650–700 nm even after the aging period. Study of the thermal behavior and decomposition kinetics evidenced that the porphyrin H_2(4-TRPyP) is the least stable of the group and that all compounds decompose according to first-order kinetics.

Keywords: Sol–gel gel; Spectroscopic study; Tetraruthenated porphyrins; Hybrid material

1. Introduction

Porphyrins are known to play a significant role in several biological systems and present important optical properties [1]. In addition, the build-up of polymetallic supermolecules based on porphyrins and ruthenium–bipyridine complexes has been pursued with great interest. A relevant series of symmetric polynuclear species has been obtained by attaching four $[Ru^{II}(bipy)_2Cl^+]$ groups to the pyridyl substituents of meso-tetra-(4-pyridyl)porphyrin and its metallated derivatives [2]. These compounds display a rich electrochemistry and versatile catalytic and photochemical properties associated with the ruthenium–bipyridine and metalloporphyrin complexes [3–7]. In addition, the porphyrins studied here have been previously described as active species for electrochemical sensing of nitrite and sulfite in solution [3].

The chemistry of polymetallic porphyrins and supermolecules has attracted the attention of researchers interested in the development of molecular devices and catalysts for several processes [8]. The development of a device based on those active porphyrins would be accomplished by the development of an appropriate matrix, but a challenge in this case is to find a host for porphyrin incorporation at temperatures where the guest molecules are stable. Several groups have reported the advantages of the sol–gel method for porphyrin insertion, such as the feasibility of monoliths with good quality and preparation at low temperatures ensuring thermal stability of the guest molecules [9,10]. However, some drawbacks found in this field are related to the low solubility of many porphyrins in polar solvents such as water and alcohols, which precludes their incorporation into silica gels [11]. This problem has been overcome by the attachment of chemical substituents such as –OH and $–NH_2$ in the peripheral groups of the macrocycles [12]. In other cases, porphyrin aggregation, fluorescence suppression upon aging, and demetallation of metallated porphyrins un-

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[*] Corresponding author. Fax: +55 7932126651.
E-mail address: ledjane@ufs.br (L.S. Barreto).

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der acidic conditions of the sol–gel procedure were described, making necessary the choice of a suitable solvent mixture to solve these problems [13]. Thus, the preparation of porphyrin containing sol–gel monoliths is not always free from complications, but in this work we present a porphyrin family that is particularly suitable for incorporation into sol–gel matrices. The presence of four $[\mathrm{Ru^{II}(bipy)_2Cl^+}]$ groups bound to the pyridyl center greatly improves the solubility and stability of the tetraruthenated porphyrins [14]. Such complexes are rather stable and inert, imparting convenient structural characteristics to the supramolecular species, and also a wide variety of functional aspects from their rich chemistry [15,16].

The present work reports a spectroscopic study of fluorescent tetraruthenated porphyrins H_2(3-TRPyP) and H_2(4-TRPyP) in an SiO_2 matrix produced by sol–gel techniques. A metallated porphyrin Co(3-TRPyP) was also incorporated to test for possible demetallation. Finally, considering that the thermal behavior of the material is an important property to be evaluated prior to any practical application, the thermal decomposition of the tetraruthenated porphyrins is described by comparative application of kinetic methods.

2. Experimental

2.1. Materials

Analytical grade tetraethyl orthosilicate (TEOS), pyridine, and anhydrous ethyl alcohol were purchased from Sigma. All porphyrins were synthesized as described in Ref. [4].

2.2. Preparation of the sol–gel gels

The SiO_2 gels were prepared by the sol–gel method according to the following procedure. Briefly, TEOS, distilled water, and pyridine were mixed together in a 1.00:4.00:0.02 mol proportion, followed by addition of 1 mol/L HCl solution to adjust the pH to 1. Finally, at this point, 1 mL of 1×10^{-5} mol/L alcoholic solutions of the porphyrins H_2(3-TRPyP), H_2(4-TRPyP), or Co(3-TRPyP) was added to the reaction mixture and the gel obtained was stirred for 72 h protected from light, aged for 15 days, and dried for 96 h at 65 °C.

2.3. Characterization of the samples

The samples have been characterized by UV–visible absorption spectroscopy in the range 200–800 nm using a Perkin–Elmer Lambda 45 UV/vis spectrophotometer. The emission and excitation spectra were obtained using a Perkin–Elmer LS 55 luminescence spectrometer. Powder X-ray diffraction patterns were obtained in a Rigaku diffractometer using Cu$K\alpha$ ($\lambda = 1.54060$ Å), 40 mA, and 40 kV, at a scanning rate of 3 °C/min. The TG/DTG measurements were carried out in a TA SDT 2960 instrument under N_2 flow of 100 mL/min and at heating rates of 10, 15, and 20 °C/min.

2.4. Study of thermal decomposition

The determination of the mechanism and activation energy of thermal decomposition was performed using kinetic models usually applied to solid state reactions, such as the integration (Coats–Redfern) [17] and approximation (Horowitz–Metzger) [18] methods presented in the following equations,

$$\ln\left[g(\alpha)/T^2\right] = \ln AR/\beta E[1 - 2RT/E] - E/RT, \tag{1}$$

where $g(\alpha)$ corresponds to the chosen kinetic model function, β is the heating rate, A is the frequency factor, R is the gas constant, T is the temperature, and E is the activation energy [18], and

$$\ln\left[g(\alpha)\right] = \left[E/RT_{\mathrm{m}}^2\right]\Theta, \tag{2}$$

where T_{m} is the temperature of maximum conversion rate and $\Theta = T - T_{\mathrm{m}}$.

3. Results and discussion

XRD patterns (not shown) of all the silica gels prepared were characterized by the presence of a halo, pointing out their amorphous character. All porphyrin-containing SiO_2 samples were transparent and presented the characteristic yellow color of porphyrin alcoholic solutions, which was primary evidence of incorporation. The color as well as all spectroscopic properties showed no change over 3 years of storage under ambient conditions, indicating very high stability.

3.1. Spectroscopic properties

Figs. 1 and 2 present the absorption spectra of the sol–gel matrix in (a), the absorption spectrum of the gels containing H_2(3-TRPyP) and H_2(4-TRPyP) in (b), and the emission spectra of the gels containing H_2(3-TRPyP) and H_2(4-TRPyP) in (c). In Fig. 3 the absorption spectrum of the sol–gel matrix is presented in (a), along with the absorption spectrum of the gel containing the porphyrin Co(3-TRPyP) in (b). Band assignments for the porphyrins in the gel are described in Table 1.

The electronic spectra of the porphyrins encapsulated in the silica gels are consistent with the solution spectra described in Refs. [4–6], which is strong evidence of the absence of aggregation or protonation by HCl, used as catalyst for TEOS hydrolysis during the sol–gel process. For all samples the absorption spectra shows bands around 290 and 340 nm associated to the $p\pi \rightarrow p\pi^*$ transitions of bipy and a ligand field transition from $[\mathrm{Ru^{II}(bipy)_2Cl^+}]$ fragments, respectively. The band near 430 nm is attributed to the Soret transitions and small

Table 1
Electronic spectroscopic data for tetrapyridylporphyrins in silica gel

Complex	$\pi - \pi^*_{\mathrm{bipy}}$	LF	SORET	β
H_2(3-TRPyP)	291	336	433	562
H_2(4-TRPyP)	291	347	432	557
Co(3-TRPyP)	291	339	437	550

Note. LF—ligand field transition.