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Lanthanide tetrasulfophthalocyanines incorporated to SiO$_2$ gels

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Abstract The sandwich-type lanthanide phthalocyanines, HLn(Pc)$_2$, are macrocyclic molecules with important optical properties. New routes are proposed to successfully trap soluble substituted phthalocyanines in SiO$_2$ materials prepared by the sol-gel method. Specifically, the phthalocyanines studied in this work are lanthanide 2, 9, 16, 23–*bis*tetrasulfophthalocyanines, HLn(TSPc)$_2$, where Ln = Sm, Eu, Dy and Ho, and they were trapped in silica networks. The design routes to trap and bind the macrocycles into the inorganic matrix pore systems are described here. These considerations show that interesting materials with potential applications in electronic, optics and catalysis can be obtained.

Keywords Phthalocyanine · Sol-gel · Monolith · Lanthanide · Sulfo

1. Introduction

Phthalocyanines are macrocyclic molecules characterized by having 18π electron systems, which conferring them high chemical and thermal stability. For example, many phthalocyanines are known to have melting points higher that $550°C$ [1] and they are only demetalized with fuming 16 M sulfuric acid. However, the phthalocyanines suffer aggregation phenomena resulting in the loss of their desirable electrical, optical and catalytic properties.

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The first lanthanide *bis*-phthalocyanines, HLn(Pc)$_2$, were obtained by Kirin and Moskalev in 1965 [2]. Some time later, the same authors observed the change in the color of lutetium *bis*-phthalocyanine thin films when a potential of 0.01–1.0 V was applied [3]. Similar changes were observed when the pH of a lutetium *bis*-phthalocyanine solution changes from acidic to basic [4]. Nicholson and Galiardi [5] observed the interchange of the neutral, *mono* and *di*cationic species when a potential of 1.2 volts was applied to a lutetium bis-phthalocyanine. This phenomenon, called *electrochromism*, was fully studied by Nicholson and Pizarello with a neodymium phthalocyanine [6]. Katsuga and Tsutsui suggested the use of the lanthanide *bis*-tetrasulfophthalocyanines, HLn(TSPc)$_2$, as acid-base indicators [7, 8].

The sol-gel method is of great importance because of its wide applications in catalysis, optics and in sensing devices; for example, rare earth ions have been incorporated into microporous silica gels [9–11]. Likewise, it is known that phthalocyanines are insoluble in common solvents, but the presence of substituents such as sulfo (–SO$_3$H) and carboxyl (–COOH) groups placed on the periphery of the macrocycle makes them soluble in polar solvents [7, 8, 12].

Lanthanide 2, 9, 16, 23-*bis*-tetrasulfophthalocyanines, HLn(TSPc)$_2$ (Fig. 1) are water soluble macrocyclic compounds with important magnetic, electrical and optical properties [13–15].

The aqueous solutions of HLn(TSPc)$_2$ species (where Ln = Sm, Eu, Dy and Ho) show a blue or green fluorescent emission in which the wavelength maxima and the intensities depend on the corresponding lanthanide. Frequently, it is interesting and useful to make use of the luminescent properties of the HLn(TSPc)$_2$ complexes, when they can be trapped in an M$_x$O$_y$ network by using sol-gel techniques.
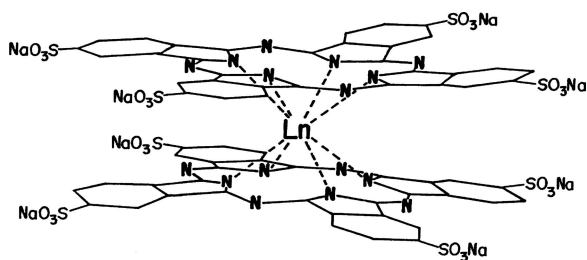
Fig. 1 Structure of tetrasodium salt of the lanthanide 2, 9, 16, 23-bistetrasulfophthalocyanine complex, HLn(TSPc)$_2$ (Ln = Sm, Eu, Dy and Ho).

In the present work we report the synthesis of lanthanide 2, 9, 16, 23-*bis*tetrasulfophthalocyanines, HLn(TSPc)$_2$, (where Ln = Sm, Eu, Dy and Ho) and their covalent bonding with the functionalized alkoxide 3-aminopropyltriethoxysilane (APTES) as a precursor, with their subsequent inclusion into SiO$_2$ gels obtained by the sol-gel method.

2. Experimental

The lanthanide 2, 9, 16, 23-*bis*tetrasulfophthalocyaninates HLn(TSPc)$_2$ (Fig. 1), were synthesized by a route that combines the methods of Weber [16] and Tsutsui [7, 8], using lanthanide acetates Ln(ac)$_3$ (Ln = Sm, Eu, Dy and Ho) and 4-sulfophthalic acid. To chemically bind the sulfo and amino groups of HLn(TSPc)$_2$ and the functionalized alkoxide 3-aminopropyltriethoxysilane (APTES), respectively, a [1:20] molar mixture of the latter compounds was refluxed at 70°C under a N$_2$ atmosphere. The reaction was monitored in a Perkin Elmer Paragon 1000 IR spectrometer for approximately 3 h. To obtain the monolithic gels, it was necessary to prepare gelling mixtures with the following molar concentration ratios: [TEOS:H$_2$O:HCl:HLn(TSPc)$_2$-APTES:DMF(or Py)] = [1:0.68:0.08:1 × 10^{-5}:0.21], where HLn(TSPc)$_2$-APTES represents pthalocyanine covalently bonded to the functionalized alkoxide. This solution was prepared by mixing (a) 0.3 mL of HLn(TSPc)$_2$-APTES solution with; (b) 2.87 mL of a homogeneous mixture of TEOS (1.38 mL) and HCl (1.49 mL of a 0.01 M solution); (c), 0.74 mL of water; and (d) 0.09 mL DMF or Py; to give a final volume of 4.0 mL. The gelling mixtures were placed in plastic cells, covered with *parafilm* and monitored by UV-visible spectroscopy with a Varian Cary 5E spectrophotometer. After monoliths were dried, they spontaneously separated from the cell walls. Samples were dried at room temperature for two weeks. The final monoliths were then dried for 24 h at 100°C. All samples were characterized by UV-Visible, NIR, IR and fluorescence spectroscopy and by powder X-ray diffraction and scanning electronic microscopy (SEM).

3. Results and discussion

The UV-visible spectra of the synthesized and purified 2, 9, 16, 23-*bis*-tetrasulfophthalocyanines of the lanthanide elements (Eu, Sm, Dy and Ho), were characterized by a Soret band at 350 nm and the most intense Q$_{III}$ band at 670 nm [2–8]. These signals are assigned to the a$_{2u}$ → e$_g(\pi*)$ and a$_{1u}$ → e$_g(\pi*)$ transitions of the macrocycle. The characteristic *sandwich* structure of the lanthanide *bis*-phthalocyanine complex macrocycles, HLn(TSPc)$_2$ is shown in Fig. 1. Aqueous solutions of HLn(TSPc)$_2$ species exhibit fluorescence whose blue-green color depends on the lanthanide identity. For example, the fluorescence spectra of the HSm(TSPc)$_2$ and HEu(TSPc)$_2$ aqueous solutions (λ_{exc} = 370 nm) show maxima at 516 nm and 511, respectively.

When the mixtures of APTES and HLn(TSPc)$_2$ were heated under an N$_2$ atmosphere, the *amino* group of APTES plays the role of nucleophile, attacking the *sulfo* group (–SO$_3$H) to form a *sulfamide* group (–SO$_2$–NH–), as can be seen in Fig. 2.

Figure 3 shows the FTIR spectra of (a) APTES; (b) the APTES-HEu(TSPc)$_2$ mixture heated at 70°C for 30 min; and (c) the same mixture heated at 70°C for 120 min. The absorption peaks appearing at 2973, 2926 and 2884 cm^{-1} are assigned to the antisymmetric and symmetric –CH$_2$ stretching vibrations. The peaks at 1482, 1443 and 1390 cm^{-1} correspond to –CH$_3$ and –CH$_2$ bending vibrations. The signal at 1103 cm^{-1} is assigned to the Si–O band stretching vibration and the bands at 958 and 790–796 cm^{-1} are attributed to the antisymmetric and symmetric –Si–OC$_2$H$_5$ stretching modes, respectively. The two bands at 3300 and 3376 cm^{-1} are due to the stretching modes of the –NH$_2$ group (primary amine). These latter bands represent, respectively, the antisymmetric and symmetric N–H stretching vibration. The bands are shifted to longer wavelengths by hydrogen bonding. The bands at 1596 and 875 cm^{-1} correspond to the N–H bending vibrations of the primary amine.

From the FTIR spectra of the reaction products obtained from APTES and HLn(TSPc)$_2$ (Figs. 3b and 3c), we observe that the antisymmetric and symmetric stretching vi-
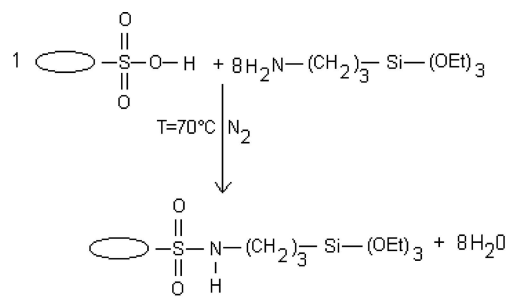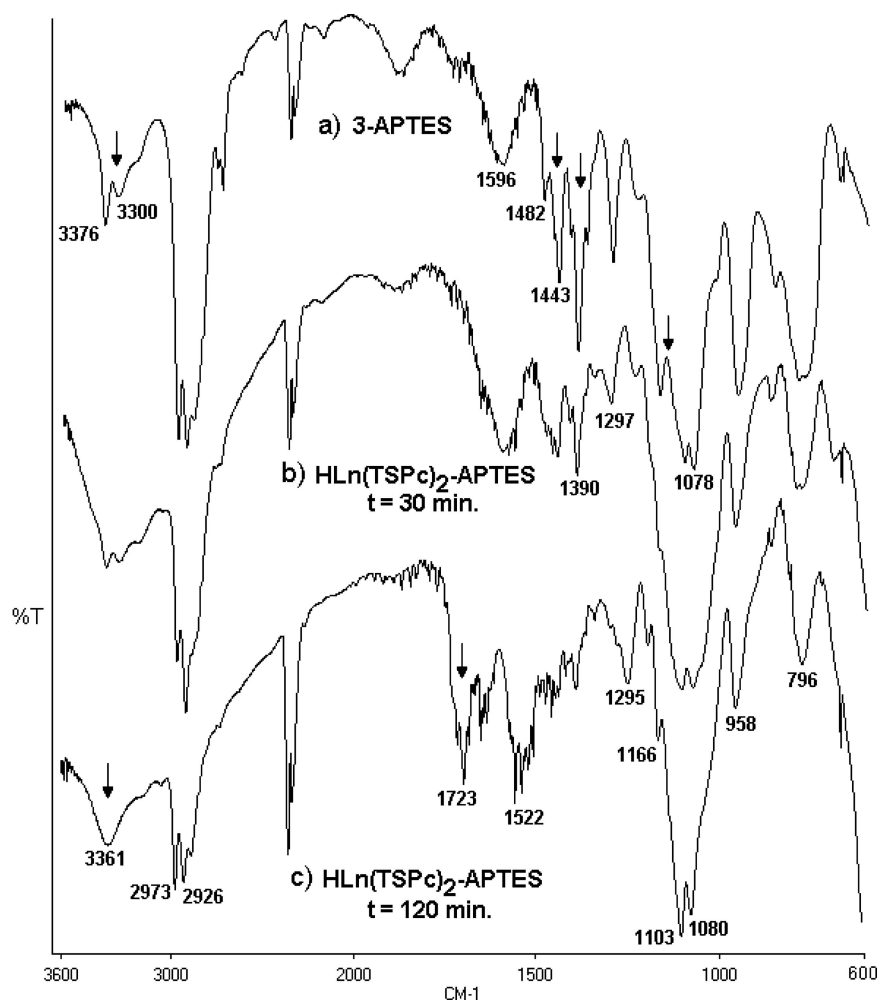

Where ⬭ represent the phthalocyanine macrocycle

Fig. 2 Proposed reaction to obtain the precursor HLn(TSPc)$_2$-APTES.

Fig. 3 FT-IR spectrum of: a) APTES, b) the monitoring of the reaction of APTES and HEu(TSPc)$_2$ at 70°C after 30 min and c) after 120 min of reaction.

brations of the –NH$_2$ group (3300–3400 cm^{-1}) are shifted, and after 120 min of reaction we observe a single band near 3361 cm^{-1}, corresponding to the stretching vibration of a secondary amine (Fig. 3c). The bands at 1596 and 875 cm^{-1} in the spectra of HLn(TSPc)$_2$-APTES are similarly modified (Figs. 3b and 3c). Moreover, the appearance of new modes at 1390 and 1166 cm^{-1}, assigned to stretching vibrations of the –O$_2$S–NH group, confirm the formation of *sulfonamide* groups.

The band at 1295 cm^{-1}, assigned to the C–N stretching vibration of the APTES amine group, essentially disappears after 120 min of reaction and the C–N stretching band observed at 1078 cm^{-1} in the APTES spectrum is shifted slightly to 1080 cm^{-1} when APTES reacts with the phthalocyanine. The conversion from primary to secondary amine is due to the formation of –O$_2$S–NH– species from the *sulfo* groups of the 2, 9, 16, 23-*bis*-tetra-sulfophthalocyanine and the amine group of APTES. The bands of APTES overlap the majority of the bands of the macrocycle, due to the higher concentration of APTES in the reacting mixture, but some bands associated with the macrocycle (including the C = C ring stretching and bending modes at 1522–1723 cm^{-1} and

668 cm^{-1}, respectively and the C = N and C–N stretching bands) are observed at the end of the reaction, when the gel appears.

The changes observed in the FTIR spectra of the other lanthanide complexes during reaction with APTES are very similar to those reported in Fig. 3 for the HEu(TSPc)$_2$-APTES system.

After the gelling mixtures separated from the walls of the plastic cells, the solid samples were dried slowly at room temperature and then at 70°C and 120°C. The monolithic gels finally obtained were strong and transparent, with X-ray diffraction patterns consistent with amorphous materials.

In the fluorescence spectra of the HEu(TSPc)$_2$ and HSm(TSPc)$_2$ species in aqueous solution (λ_{exc} = 370 nm) the band maxima are seen at 511 and 520 nm, respectively. However, the emission bands in the corresponding monolithic gels are blue-shifted by around 40 nm, and are observed at 470 nm and 480 nm in the HEu(TSPc)$_2$ and HSm(TSPc)$_2$ gels, respectively (Fig. 4).

This phenomenon is caused by the closed environment around the macrocyclic molecules and the lower polarity of the remaining liquid media in the interior of the gel pores.
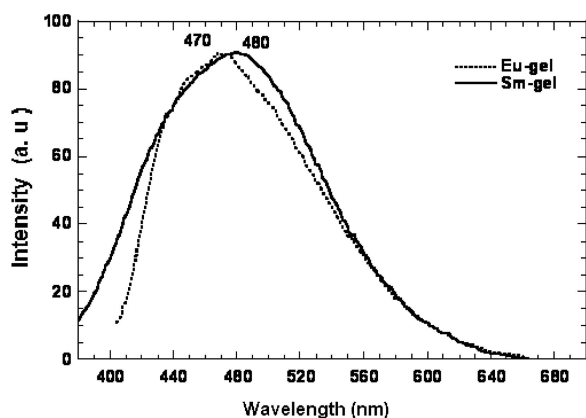
Fig. 4. Fluorescence spectra of monolithic gels prepared with the HEu(TSPc)$_2$ and HSm(TSPc)$_2$ species covalently bonded to the silica network

The lower polarity is due to the DMF used in the gelling mixture as a drying control agent. With other metal phthalo-cyanines, the DMF acts as an aggregation control agent, but in the case of the HLn(TSPc)$_2$ species, dimer formation is inhibited by steric interactions between the macrocycles and substituents of the complex. Moreover, in the case of the HLn(TSPc)$_2$-APTES species, aggregation is inhibited by the strong steric hindrance caused by the eight 3-*sulfamide-propyltriethoxysilane* ($-O_2Si-NH_2-(CH_2)_3-Si-(OC_2H_5)_3$) groups located on the periphery of the lanthanide macro-cyclic complex. Preliminary results obtained with SEM show that the monoliths obtained are homogeneous materials composed of aggregated particles with a size of 0.25 μm. The pore size distribution (determined by BET) confirmed that the macrocyclic complex could be retained within the interior pore network of the gel.

The HEu(TSPc)$_2$ and HSm(TSPc)$_2$ species trapped and covalently bonded to the silica network allow their efficient use in optics. In all cases, the emission bands showed that the fluorescence properties of the sandwich lanthanides complexes are retained in the inorganic silica network.

4. Conclusions

The lanthanide bis-tetrasulfophthalocyanine complexes, HLn(TSPc)$_2$ (Ln = Sm, Eu, Dy and Ho), were synthesized and covalently bonded to the silica network by a sol-gel procedure, involving the use of functionalized alkoxides such as 3-aminopropyltriethoxysilane (APTES). The optimal gelling mixtures were identified and the monolithic gels thus obtained are physically strong and transparent. In this way, the macrocyclic complexes inserted in the silica network retain their blue fluorescence, but shifted around 30 nm to the red.

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