Effects of the Covalent Bonding Entrapment of Tetrapyrrole Macrocycles inside Translucent Monolithic ZrO₂ Xerogels

Eduardo Salas-Bañales, R.Iris Y. Quiroz-Segoviano,

Fernando Rojas- González, Antonio Campero, Miguel A. García-Sánchez*

Department of Chemistry, Universidad Autónoma Metropolitana-Iztapalapa, Av. San Rafael Atlixco
186, Vicentina, México D. F. 09340, P. O. Box 55-534, México.

*Corresponding author e-mail: mags@xanum.uam.mx,

Tel.: +52-55-5804-4677; Fax: +52-55-5804-4

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Abstract. While searching for adequate sol-gel methodologies for successfully trapping in monomeric and stable form either porphyrins or phthalocyanines, inside translucent monolithic silica xerogels, it was discovered that the interactions of these trapped tetrapyrrole macrocycles with Si-OH surface groups inhibit or spoil the efficient display of physicochemical, especially optical, properties of the confined species. Consequently, we have developed strategies to keep the inserted macrocycle species as far as possible from these interferences by substituting the surface -OH groups for *alkyl* or *aryl* groups or trapping these species inside alternative metal oxide networks, such as ZrO₂, TiO₂, and Al₂O₃. In the present manuscript, we present, for the first time to our knowledge, a methodology for preserving the spectroscopic characteristics of metal tetrasulfophthalocyanines and cobalt tetraphenylporphyrins trapped inside the pores of ZrO₂ xerogels. The results obtained are contrasting with analogous silica systems and demonstrate that, in ZrO₂ networks, the macrocyclic species remain trapped in stable and monomeric form while keeping their original spectroscopic characteristics in a better way than when captured inside silica systems. This outcome implies a lower hydrophilic character linked to the existence of a smaller amount of surface hydroxyl groups in ZrO₂

networks, if compared to analogous SiO₂ xerogel systems. The development and study of the possibility of trapping or fixing synthetic or natural tetrapyrrole macrocycles inside inorganic networks suggest the possibility of synthesizing hybrid solid systems suitable for important applications in technological areas such as optics, catalysis, sensing and medicine

Introduction

Tetrapyrrole macrocyclic compounds are molecules that perform transcendental functions in nature, since these species constitute the main part of molecules such as chlorophyll, blood (*heme* group), cyanocobalamine (Vitamin B₁₂), and cytochromes [1-3]. Some other important compounds of this type are synthetic tetrapyrrole macrocycles, such as porphyrins (H₂P), phthalocyanines (H₂Pc), and naphthalocyanines (H₂Nc). The extensive delocalized π -electron clouds of these centrosymmetric compounds confer upon them, in addition to high chemical and thermal stabilities, other interesting spectroscopic, optical, and electrical properties that has lead to a great deal of applications in fields such as optics [4], electrochemistry [5], catalysis [6, 7], and sensing [8, 9]. Porphyrins are aromatic compounds derived from porphin (Fig. 1a), which is formed by four pyrrole rings bonded together through *methine* (=CH) groups and central or *pyrrolic* hydrogens. These last elements can be substituted by a cation to render stable metalloporphyrins; i.e. porphyrinic complexes which can allocate practically all metallic elements of the periodic table [2, 3]. In *meso*-porphyrins one or several methinic hydrogens are substituted by *alkyl* or *aryl* groups, as for instance, phenyl species in tetraphenylporphyrins (H₂TPP) (Fig. 1b).

It is well known that a better penetration of visible light into biological tissues occurs when using wavelengths in the red and infrared region, i.e. from 600 to 1500 nm [10, 11]. Many porphyrin metal-free bases (i.e. the unmetalled porphyrinic species) exhibit a red fluorescence between 600 and 730 nm. Additionally, some substituted porphyrins are selectively adsorbed by either malignant tissues or some kinds of bacteria [12] and thus employed to destroy or kill them through

Photodynamic Therapy (PDT), specifically by means of singlet oxygen $O_2(a^1\Delta_g)$ atoms generated through the incidence of red laser light [2, 3, 13, 14]. The extended π -electron conjugate system of pththalocyanines confer upon them high thermal and chemical stabilities, among other outstanding physicochemical properties [15], which are advantageous in catalysis [6, 16], optics [17], optoelectronics [18], and medicine [19].

Many times, in order to take a better advantage of the above mentioned properties, tetrapyrrole macrocyclic species require to be trapped or fixed inside the pores of solid supports, such as graphite, hydrotalcites, zeolites, metal oxide or polymer networks. Because of the organic nature of macrocycles, these molecules cannot be trapped via the traditional thermal diffusion method since impregnation alone renders scarcely concentrated and heterogeneous systems. Contrastingly, the sol-gel method (also known as "*chimie douce*" [20, 21] or soft chemistry) has made possible the trapping of chemical species that range from either simple cations [22] or organic moieties [23] to whole bacterial systems [24].

The spectroscopic characteristics assumed by confined phthalocyanines help to understand the changes that occur in sol-gel systems during a macrocycle entrapping process. The plan developed on grounds of this strategy consisted in using aluminum μ -hydroxy-tetrasulphophthalocyanine, (OH)AlTSPc (Fig. 1c) as a tracer species to monitor the enclosing (gelling) macrocycle process through UV-Vis spectroscopy. This molecule was selected due to its aqueous solubility, its remarkable thermal and chemical stabilities, and its low propensity to form aggregates (i.e. flocculi or coagula) and because of the good stability of the respective UV-Vis and fluorescence spectra along an extensive range of pH values. It is also important to establish that this molecule is preferentially physically (while not chemically) adsorbed thus resulting very helpful for determining the optimal conditions required to reach a disaggregated physical (or even chemical) inclusion, within translucent monolithic silica xerogels, of diverse metallic complexes of

tetrasulphthalocyanine, MTSPc, [25-27], porphyrin free bases [28], and diverse porphyrinic complexes [29].

Fig. 1. Structures of porphyrin tetrapyrrolic macrocycles. (a) Bond lengths, angles and positions (1 to 20) of possible peripheral substituents; (b) ortho, meta and para positions in tetraphenylporphyrin (H₂T(o-, m-, p-S)PP); (c) chemical structure of a metallic complex of tetrasulfophthalocyanine, MTSPc.

Nevertheless, in the previously mentioned systems, the molecular interactions of tetrapyrrole macrocycles with the surface of the silica pore network (principally with Si-OH groups) inhibit the efficient display of the chemical and spectroscopic properties of entrapped macrocyclic compounds [28, 29]. In order to diminish these undesirable phenomena [27, 30-32] some strategies have been proposed and explored. These strategies comprise actions to separate, as far as possible, the macrocycle species from the pore network walls through the establishment of long covalent unions, which are generated by substituting the surface Si-OH groups for alkyl or aryl groups or by trapping the macrocyclic species inside networks containing, instead of SiO₂, metal oxides such as ZrO₂, TiO₂, Al₂O₃, etc.

The location of macrocyclic species far from the pore walls has been made possible through the use of functionalized alkoxides and organic functions inserted at the periphery of the respective macrocyclic species. Through this methodology, systems containing trapped macrocycles can preserve the original fluorescence of the precursory tetrapyrrole molecules, thus keeping them in a similar condition as that displayed in solution by the free (unlinked) species [30, 31]. In a similar way, substitution of Si-OH groups by alkyl or aryl groups proceeding from the addition of organo-substituted alkoxides produce solids systems in which the trapped or fixed macrocyclic species display, in a better fashion, their coordination and luminescent properties. Furthermore, in these systems the intensity of the UV-vis and fluorescence signals of macrocyclic species depends on the *alkyl* or *aryl* groups attached to the pore network [27, 32]. Apparently, the presence of organic chains attached to the pore walls induces an internal physicochemical environment in which the electronic transitions of the trapped macrocycles occur in an easier way. Through this procedure, it has been possible to optimize the fluorescence of synthetic porphyrins and, more recently, that of natural tetrapyrrole macrocycles, such as chlorophyll *a* [33]. In the present manuscript, we show the first results concerning the possibility of optimizing the displaying of physicochemical properties of macrocyclic species trapped or bonded inside inorganic networks that are different from SiO₂, particularly inside ZrO₂ xerogels, prepared by the sol-gel method.

It is well known that zirconium oxide possesses interesting physicochemical properties, such as great hardness, high fusion point, low thermal expansion coefficient (10^{-5} K^{-1}), a thermal conductivity two orders of magnitude lower than that of common metals ($2.09 \text{ W m}^{-1} \text{ s K}$), a high refraction index of 2.21 (with $\lambda = 630 \text{ nm}$), a low absorption coefficient, together with a narrow band gap (3.8 to 3.2 eV). Because of these properties, zirconium oxide results to be an interesting option for developing thin films, sensors, photoreactive materials, protective barriers, and optical applications such as waveguide materials [34].

Due to its convenient properties, the (OH)AlTSPc species was chosen as a spectroscopic tracer or probe to determine the optimal conditions required to synthesize translucent and monolithic ZrO_2 xerogels having tetrapyrrole macrocyclic species physically trapped or covalently fixed (in a disaggregated and stable form) within the pores of xerogel networks.

Experimental

Synthesis of Macrocyclic Compounds. Tetrasulphophthalocyanine metal complexes, MTSPc (where $M \equiv \text{Fe, Co, Ni, Cu and Al}$), were synthesized by the Weber and Busch method [35]. From cobalt chloride, CoCl_3 , and tetra-(para-carboxyphenyl)porphyrin metal-free base, $\text{H}_2\text{T}(p\text{-COOH})\text{PP}$, the respective cobalt tetra-(para-carboxyphenyl)porphyrine, $\text{CoT}(p\text{-COOH})\text{PP}$ was obtained. The $\text{H}_2\text{T}(p\text{-COOH})\text{PP}$ free base was prepared from pyrrole and *p*-carboxy-benzaldehyde through the Rothmund [36] reaction, while following the Adler methodology [37]. The ensuing macrocyclic compounds were characterized by UV-Vis, FTIR, elemental analysis, and NMR.

Macrocycle Trapping via Covalent Bonding Inside ZrO_2 Pore Networks. ZrO_2 pore networks were prepared from zirconium tetrapropoxyde, $(\text{Zr}(\text{OPr}^n)_4)$, dissolved in propylic alcohol (HOPr^n), whose reactivity was regulated through coordination with acetylacetone (acac). By using (OH)AlTSPc as a probe species, it was determined that an optimal $\text{Zr}(\text{OPr}^n)_4$: H_2O : HOPr^n : acac sequence of molar ratios equivalent to 2: 4: 8: 1 guarantees the creation of translucent and monolithic ZrO_2 xerogels that allow macrocyclic species to be trapped inside the pore network in a monomeric (disaggregated) and stable form. The addition of a small amount of dimethylformamide (DMF), as dry control agent, produces hard, fractureless monoliths. The Zr gelling mixture is prepared from a solution of 0.42 mL of acetylacetone in 1.2 mL of 1-propanol, which is added to the solution of the macrocycle species dissolved in 0.625 mL of water and 0.083 mL of DMF. Finally, 3.6 mL of a solution at 70% v/v of $\text{Zr}(\text{OPr}^n)_4$ in 1-propanol was added dropwise.

By observing the above optimal composition of molar ratios determined for the adequate inclusion of (OH)AlTSPc molecules within ZrO_2 xerogels, it was possible to physically entrap within ZrO_2 pore networks, different MTSP complexes (where $M \equiv \text{Fe, Co, Ni, Cu, and Al}$), all in monomeric and stable forms. Moreover, CoT(p-COOH)PP , a tetra-(*para*-carboxi-tetraphenyl)-porphyrin, was covalently bonded to the ZrO_2 pore walls through the bridging action of 3-amino-propyl-triethoxysilane (APTES) (Fig. 2). In order to perform this action, it was first necessary to synthesize the respective CoP-F hydrolyzable precursor through the chemical union of carboxyl groups of porphyrin with amine groups of APTES (Fig. 2). In a second step, the CoP-F precursor was covalently bonded to the Zr network through hydrolysis and polycondensation reactions between the ethoxy groups of APTES and the propoxyde species of the $\text{Zr(OPr}^n)_4$. To perform this linking action 0.3125 mL of precursor was combined with 0.625 mL of H_2O and mixed with the necessary volumes of $\text{Zr(OPr}^n)_4$, HOPr^n , Hacac, according to the same molar ratio as established before. After gellification, the samples were dried for a week at room temperature, afterward kept at 75°C for 1 day and finally at 125°C for one more day. At the end of this process, the samples were washed with water, propanol, acetone, and chloroform to eliminate unbounded porphyrin. All samples were next characterized by FTIR, UV-Vis and NIR spectroscopy, as well as by X-ray powder diffraction, N_2 adsorption, HRSEM, and EDS.

Fig. 2. Reaction scheme for the covalent union of cobalt tetra-(*p*-carboxy-phenyl)-porphyrin, $\text{CoT}(\text{p-COOH})\text{PP}$, to the ZrO_2 network.

Instrumentation. UV-visible and near infrared (NIR) characterization were carried out in a Cary–Varian 500 E device, Infrared spectra (FTIR) were obtained from a Perkin-Elmer GX FTIR instrument. Nuclear Magnetic Resonance Spectroscopy was accomplished via a Bruker Advance +300 spectrometer working at 500 MHz. In turn, HRSEM images were recorded by means of a JEOL 7600F microscope equipped with an Oxford Instruments INCA EDS detector. N_2 adsorption-desorption isotherms were measured in a Micromeritics ASAP 2020 instrument at 76 K (boiling point of N_2 at México City’s 2250 m altitude). Pore size distributions (PSD), inherent to the ZrO_2 matrix entrapping macrocyclic species, were calculated by the NLDFT method applied to the boundary desorption curve of the N_2 isotherms [38] while assuming spherical pore cavities.

Results and Discussion

As mentioned before, the (OH) ALTSPc species was used to determine the optimal sol-gel experimental conditions required to synthesize translucent monolithic ZrO_2 xerogels for encapsulating tetrapyrrole macrocyclic species in disaggregated and stable form. To find these optimal conditions, the molar concentration of (OH)ALTSPc in water solution was set as 4.04×10^{-3}

M. Once that diverse combinations of experimental concentrations were explored, it was found that an [acac: $\text{Zr}(\text{OPr}^n)_4$: H_2O : HOPr^n] molar ratio sequence equivalent to [2: 4: 8: 1], was the most adequate for the purpose of preparing ZrO_2 monolithic, translucent xerogels. In the above gelling mixture, the addition of acetylacetone becomes necessary in order to reduce the hydrolysis and condensation reaction rates through the formation of a zirconium complex (i.e. essentially the $\text{Zr}(\text{OPr}^n)_3\text{acac}$ adduct species). In this way, it was possible to prepare ZrO_2 translucent porous xerogels in which the macrocyclic species was trapped in stable and monomeric form. To verify this claim, the spectroscopic characteristics of the (OH)ALTSPc molecules were monitored to assess their physicochemical situation inside the ZrO_2 pore network.

As it is already well known, a typical UV-Vis spectrum (Fig. 3a) of a single metal phthalocyanine displays a most intense Q_{II} band, which is assigned to an $a_{1u}(\pi) \rightarrow e_g(\pi^*)$ transition occurring at around 679 nm; and a less intense Soret band (B) located at about 347 nm and that has been ascribed to an $a_{2u}(\pi) \rightarrow e_g(\pi^*)$ transition [15]. A weak Q_{IV} satellite band (of a vibrational nature) was also observed at around 610 nm. Importantly, when phthalocyanine molecules form dimers, as happens with the CuTSPc molecule, the respective UV-vis spectrum displays only two bands: a B band at around 337 nm and a Q_{II} band at 629 nm. As can be seen in the UV-vis spectra of two samples containing (OH)ALTSPc trapped inside ZrO_2 xerogels, one including and another not including DMF as dry control agent, the resulting characterization pathways correspond to monomers with their principal bands appearing at 680 and 613 nm (Fig 3b). Apparently, there exists no great effect of DMF over the stability and possible aggregation of the (OH)ALTSPc species; nevertheless, xerogels obtained in the presence of this last additive result more rigid and without fractures. In these spectra, the Soret band, that appears at around 347 nm in the (OH)ALTSPc solution, prevailed although somewhat concealed by a wide ZrO_2 peak (i.e. a signal centered at around 360 nm).

Fig. 3. (a) UV-Vis spectra of monomeric (OH)AITSPc species and aggregates of CuTSPc in aqueous solution. (b) UV-Vis spectra of a pristine ZrO₂ xerogel (blank) with the (OH)AITSPc species trapped inside the pores and employing or not DMF as dry control agent.

In order to identify the nature of the NIR bands of ZrO₂ xerogels, the rehydration process of this substrate was followed for about 100 hours. In Figure 3a the bands at 1390 and 2270 nm were substituted or masked by those emerging at 1422 and around 2300 nm. Additionally, the absorbance displayed by the band at 1930 nm increased with time. These changes resulted to be very similar to those observed in sol-gel systems synthesized from pristine silica (Fig. 4b). For these reasons, the

bands at 1390 and 2270 nm can be associated with remnant Zr-OH groups; in turn, the band at 1930 nm can be linked to physisorbed water while the bands that are merging with time, and appearing at 1422 and 2300 nm can be related to Zr-OH groups interacting through hydrogen bonds with the physisorbed water. Finally, the bands at 1622 and 1729 can be due to $-\text{CH}_2-$ chains still bonded to the network, as remnant *propoxy* groups ($-\text{OPr}$). Furthermore, the rehydration process occurs faster in silica than in ZrO_2 thus suggesting the existence of a lesser interconnected pore network or a weaker hydrophilic nature of the zirconium oxide matrix.

Fig. 4. (a) NIR monitoring of ZrO_2 during water rehydration. (b) rehydration of silica networks, after treatment at 225°C .

Consequently, in the NIR spectra of ZrO_2 samples entrapping (OH)AITSPc species (Fig. 5), the band observed at 2268 nm can be attributed to the Zr-OH vibrations. The couple of less intense bands appearing at 1683, and 1731 nm are related to Zr-O-CH₂- vibrations, *i.e.* to the presence of remaining acetylacetone or/and propoxyde (-OPr) groups in the pore network. Additionally, a signal that reveals the presence of physisorbed water in the network is observed at 1929 nm and bands at around 1426 and 2305 nm are due to Zr-OH vibration groups interacting with water. The spectra of pristine (OH)AITSPc and the ZrO_2 xerogel containing it, are very similar to each other but the signal pathway of the sample synthesized with DMF displays more intense bands. This difference reveals the existence of a higher amount of water in this sample as a consequence of the presence of DMF.

Fig. 5. NIR spectra of a pristine ZrO_2 xerogel (blank) and xerogel samples encapsulating $(\text{OH})\text{AITSPc}$ species in the presence or absence of DMF.

The HRSEM images in Figure 6 show a ZrO_2 xerogel sample of a fractured texture with no evidence (because of insufficient resolution) of the existence of great pore cavities. Furthermore, in the same figure EDS mapping reveals a homogeneous distribution of Al, C and Zr elements, which can be associated to the presence of an aluminum phthalocyanine complex uniformly trapped inside the ZrO_2 network. From EDS analysis, the following surface element contents are obtained: 0.37 % of Al (1.00 mol), 1.31 % N (6.82 mol), 16.33 % C (99.14 mol), 41.4 % (188.7 mol) of O, and 40.59 % of Zr (32.45 mol). Considering that the molecular formula of the $(\text{OH})\text{AITSPc}$ complex is $\text{Al}_1\text{N}_8\text{C}_{32}\text{S}_4\text{O}_{13}\text{H}_{13}\text{Na}_4$, the percentage of Al and N can only be associated to the presence of aluminum phthalocyanine. In a similar way, 32 moles of carbon and 13 of oxygen can be associated to the phthalocyanine complex and the excess of these elements with the existence of remnant acetylacetone and *propoxy* groups (OC_3H_7). Furthermore, the O/Zr molar relation is of about 5.5 mol O/ mol Zr; this oxygen excess can be attributed to Zr-OH groups in the network. The above wt % reveals that, on the surface of the samples there exist 32 zirconium atoms per each molecule of

(OH)AlTSPc. In an ideal situation, most of these atoms are encircling the cavities in which phthalocyanine species remain trapped in stable and monomeric form.

The previous results demonstrate that macrocyclic species can be trapped in disaggregated (monomeric) and stable form inside the pores of a ZrO_2 network that is constructed around them. The next experimental step consisted in the actual entrapping of MTSPc (where M can be Fe, Co, Ni and Cu) species susceptible to aggregation. As first instance, the respective MTSPc complex was dissolved in the necessary water to fulfill the $\text{Zr}(\text{OPr}^n)_4$: H_2O : HOPr^n : acac molar mixture to be equivalent to a 2: 4: 8: 1 sequence, which renders a MTSPc concentration of 3.57×10^{-4} M. Furthermore, 0.082 mL of DMF was added as an aggregation inhibiting agent.

Fig. 6. HRSEM images of a ZrO_2 monolithic sample doped with $(\text{OH})\text{AlSPc}$ and the corresponding EDS carbon, aluminum and zirconium mapping as well as the wt. % distribution graph included.

In the UV-Vis spectra of ensuing ZrO_2 xerogels (Fig. 7), show Soret bands at around 370 to 400 nm that can be observed together with Q_{IV} and Q_{II} characteristic bands appearing at 610 and 678 nm, respectively. This set of signals corresponds to monomeric and stable structures of the MTSPc species. Once these samples were synthesized by employing the same MTSPc concentration, the intensity of the Q_{II} band decreased according to the following cation sequence: $(\text{OH})\text{CoTSPc} > \text{CuTSPc} > \text{NiTSPc} > (\text{OH})\text{FeTSPc} > (\text{OH})\text{AlTSPc}$. In these experiments the CuTSPc species, which is a complex having a high tendency to produce particle aggregates, remained trapped in stable and monomeric form inside the pores of the ZrO_2 matrix, a situation that was not attained (by a similar entrapping process of these species) inside silica pores [25, 26]. This means that MTSPc species remained solvated inside a more convenient physicochemical environment that was induced by the ZrO_2 network, which was created around these species, something that is not frequently attained in SiO_2 systems. This observation, together with the evidence arising from NIR analysis, demonstrates that the ZrO_2 matrix induces a lower polar environment around the MTSPc species, which inhibit its tendency to form aggregates while inducing stable monomeric entrapped species. Indirectly, the above mentioned evidence demonstrates the weaker hydrophilic nature of ZrO_2 and, possibly, the existence of a smaller population of M-OH surface groups, if compared to silica.

Fig. 7. UV-vis spectra of final ZrO_2 xerogel pore networks with the MTSPc species ($M = \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}$ and Al) encapsulated.

In the NIR spectra of ZrO_2 xerogels, dried at 125°C , some bands are located (Fig. 8) at around 1429 nm ; these signals can be attributed to Zr-OH vibrations at 1693 and 1738 nm because of the presence of remnant Zr-OPr groups. Interestingly, the absorbance intensity of these bands at around 1900 nm can be linked to an amount of physisorbed water, according to the following order of abundance: $\text{FeTSPc} > \text{CoTSPc} > \text{NiTSPc} > \text{CuTSPc} > (\text{OH})\text{AlTSPc}$. This means that the amount of remnant water apparently depends on the identity of the metal cation that is present in the MTSPc complex, concretely on the atomic number (z). This interesting result suggests that the capacity of water sorption, and possibly of other chemical species, depends on the identity of the cation existing in the trapped MTSPc species inside the ZrO_2 pores.

Fig. 8. NIR spectra of ZrO_2 samples with MTSPc species physically trapped inside the pores of the networks.

The ensuing N_2 sorption-desorption isotherms at 76 K of ZrO_2 xerogels containing entrapped MTSPc species, are all similar in shape to each other (Fig. 9), i.e. apparent IUPAC Type I isotherms endowed with H3 hysteresis cycles [39]. In principle, this isotherm shape is representative of microporous materials; however a pore size analysis should be performed beforehand in order to arrive to more dependable conclusions. In each case, the hysteresis cycle is very narrow thus suggesting that both condensation and evaporation of N_2 molecules occur straightforwardly without the irruption of cooperative phenomena or pore blocking effects. However, it is evident that the sorption capacity of ZrO_2 xerogels depends on the identity of the MTSPc compound trapped inside the pore network. This total uptake follows the next descending sequence: $(\text{OH})\text{AlTsPc} > \text{CuTsPc} > \text{FeTsPc} > \text{NiTsPc} > \text{CoTsPc} > \text{pristine } \text{ZrO}_2$. As it occurs in the case of physisorbed water, in the present sorption analysis N_2 sorption behavior depends on the identity of the metal cation that is present in the MTSPc species. Again, these textural results suggest that the presence of trapped macrocyclic species determines the size of the ZrO_2 cavities that are created around these species.

Fig. 9. (a) N₂ sorption-desorption isotherms (at 76K) of ZrO₂ samples containing different MTSPc species trapped inside the pore network. (b) Pore-size distributions of ZrO₂ substrates calculated by application of the NLDFT approach to desorption boundary isotherm assuming spherical pore cavities.

The average pore diameter (Φ) and the specific surface area of each substrate were calculated from the corresponding N_2 isotherm (Table 1). The average pore diameters of the ZrO_2 cavities were obtained from the Non-Local Density Functional approach [38] as applied to desorption boundary curve of the hysteresis loop of the isotherm. Spherical cavities were assumed for performing this calculation. The pore widths of the different MTSPc species encapsulating macrocyclic species ranged from 1.9 to 2.2 nm, values which were smaller, or somewhat similar, than those determined for the pristine (i.e. free of MTSPc) ZrO_2 matrix. However, these sizes were also smaller than those evaluated for analogue materials involving MTSPc species trapped inside silica networks. In this latter case, pore sizes ranged from 2.7 to 3.5 nm [25, 26]. As it is known, MTSPc species attains an approximate size of 1.8 to 2.0 nm, which results to be very similar to the ZrO_2 average pore diameters. This result suggests that pore cavity formation occurs around solvated MTSPc species and that the $-SO_3Na$ groups interact strongly with the $Zr-OH$ groups attached to the pore walls. In turn, the surface areas ranged from 32.4 to 48.3 m^2/g and resulted to be slightly higher than that of the pristine ZrO_2 sample (28.1 m^2/g).

Contrastingly, the surface areas determined for analogous silica systems ranged from 540 to 631 m^2/g [25, 26], which are significantly larger than those of the ZrO_2 materials (Table 1). It has been reported that the typical surfaces areas of ZrO_2 substrates obtained from sol-gel method and dried at room temperature correspond to about 100 m^2/g [40] and to 74 m^2/g after being dried at 450 °C [41]. These relatively low values of the surface area can just be attributed to the chemical nature of the ZrO_2 network; nevertheless, the presence of occluded MTSPc species still induces the formation of cavities in accordance with the dimensions of the trapped macrocyclic species.

Table 1. Specific surface areas and average pore widths of ZrO₂ samples containing trapped MTSPc species in their pores as evaluated from N₂ sorption.

Sample	Specific Surface Area m ² /g	V _p mm ³ /g	Average pore diameter Φ/ nm
ZrO ₂	28.12	15.65	2.2
(OH)FeTSPc/ZrO ₂	38.59	19.67	2.0
CoTSPc/ZrO ₂	32.42	17.66	2.2
NiTSPc/ZrO ₂	35.26	17.43	1.9
CuTSPc/ZrO ₂	46.14	12.37	2.0
(OH)AlTSPc/ZrO ₂	48.39	12.43	2.0

The small pore size, low total pore volume and low surface area values displayed by the ZrO₂ substrates, including or not encapsulated MTSPc species, rests on the fact that the reaction times for the hydrolysis of zirconium alkoxides have an order of magnitude of microseconds, *i.e.* 10⁵–10⁸ times quicker than silicon alkoxides [42]. This rate is responsible of the creation of very small ZrO₂ precursory nucleating centers; whose formation insides on the textural parameters and pore morphology as follows; the large number of small particles creates compact aggregates, which are not giving access to their interior volume given the very small pore throats that connect them with neighboring pore cavities. Importantly, the porous structure can evolution from depicting a Type I to a Type IV isotherm by two alternative ways: (i) by increasing the annealing temperature of the xerogel [43] or (ii) by inserting relatively large macrocyclic molecules in the xerogel network as for instance dodecyltriethoxysilane [44]. The porous structure is opened up by the evolution of volatile materials still remaining in the xerogel structure(*e.g.* acac) when the hybrid material is treated at higher temperatures or by creating or widening the interconnections established between neighboring pore cavities when the trapped molecules are large enough.

The HRSEM image of a ZrO₂ xerogel encapsulating the CoTSPc species displays a smooth surface without evident cavities (Fig. 10); *i.e.* the microscope magnification employed is not enough to perceive small nanometric holes. In turn, EDS mapping of carbon, oxygen, and zirconium reveals a homogeneous distribution of these elements on the surface of each sample. The weight percentage

determined for these elements was 27.47 % of C, 53.31 % of O, and 18.17 % of Zr. These results disclose the presence of organic materials related to the existence of a trapped macrocycle structure, as well as residual propoxy groups, and acetylacetone remnants. However, it again arise an oxygen excess that can be ascribed to the formation of an imperfect ZrO_2 network with numerous Zr-OH surface groups that provide some hydrophilic character to the substrate. In this work, we present the results for the case of a ZrO_2 xerogel system that includes trapped CoTSPc molecules, which is related to those synthesized from (OH)FeTSPc, NITSPc, and CuTSPc species.

Fig. 10. HRSEM and EDS images of a ZrO_2 xerogel with the CoTSPc species trapped inside the pores.

In order to evaluate the possibility of extending the above developed methodology to the trapping or fixing a myriad of different tetrapyrrole macrocycles, the CoT(p-COOH)PP species was chosen as an insertion probe molecule in the present investigation. Since no commercial functionalized zirconium alkoxides are offered in the market, a viable option is to make use of the available silicon alkoxides, such as 3-aminopropyltriethoxysilane (APTES) and 3-isocyanatepropyltriethoxysilane (IPTES). Then, the first step of our synthesis methodology was to establish covalent unions between

the carboxyl groups (-COOH) of porphyrin and amine groups (-NH₂) of APTES. This process rendered the respective CoP-F precursor (Fig 2). The formation of this compound was followed by FTIR spectroscopy as has been previously reported [32]. In a second step, in order to obtain the ZrO₂ xerogel, the freshly synthesized precursor was dissolved in 0.3125 mL of 1-propanol and added to a Zr(OPrⁿ)₄ : H₂O : PrⁿOH : acac molar mixture numerically equivalent to 2 : 4 : 8 : 1.

The UV-Vis spectrum of a CoT(p-COOH)PP solution depicts an intense and narrow Soret band at 434 nm while the accompanying Q_{III} and Q_{II} bands appear at 552 and 589 nm, respectively. This signal pathway is characteristic of a porphyrinic complex, such as the cobalt complex selected to pursue the present investigation (Fig 11a). Contrastingly to phthalocyanines, porphyrins are compounds that are easily protonated under an acidic medium. When these circumstances are met, the porphyrinic complex loses its central metal cation and forms a dicationic porphyrin, H₄P⁴⁺. This change is reflected in the respective UV-vis spectrum by a Soret band that is shifted toward a higher wavelength and also by the substitution of Q_{II} and Q_{III} bands by a more intense Q_I band at around 650 nm. Visually, the purple or reddish solution containing the porphyrin turns green, thus making evident the demetallation and protonation of the complex.

In the UV-Vis spectrum of the xerogel entrapping the CoT(p-COOH)PP species covalently bonded to ZrO₂ pore walls, it was observed a broad Soret band at around 438 nm while the Q_{III} and Q_{II} signals are located at 549 and 586 nm, respectively. This signal pathway was similar to that displayed by the free cobalt porphyrin in solution, then suggesting its existence as a trapped species in a monomeric and stable form; i.e., the cobalt complex bonded to the pore walls of the zirconium oxide network in a demetalled and unprotonated state,. The existence of a wide Soret band may be attributed to the interaction of the porphyrinic complex with the Zr-OH groups attached to the pore walls or to the superposition of this band with the ZrO₂ network, whose maximum intensity is observed at around 436 nm. A weak Soret band at 429 nm and two Q bands at 549 and 588 nm were

observed in the UV-vis spectrum of analogous silica systems in which the same cobalt complex could be bonded to the SiO_2 pore walls, through the bridging action of APTES (Fig 11b) [32].

The absence of traces of porphyrin complexes in the solvents employed to wash the ZrO_2 xerogel samples, together with the distinctive UV-vis signal pathways, demonstrate that, in both cases, the porphyrinic complex has been successfully bonded to the pore network in stable and monomeric form. This last observation suggests the possibility of bonding the free bases or the respective metal complexes of other synthetic or natural tetrapyrrole macrocycle, to the pore walls of inorganic networks, as the ZrO_2 , TiO_2 , Al_2O_3 , etc. The most important consequence of this finding is the opportunity of synthesizing new hybrid materials that conjugate the transcendental properties of tetrapyrrole macrocycles with the useful physicochemical characteristics of inorganic networks and employ these hybrid systems in strategic areas such as optics, catalysis, sensing, and medicine.

Fig.11. UV-Vis spectra of CoT(p-COOH)PP species in: (a) solution and (b) covalently bonded to ZrO_2 and SiO_2 pore networks.

HRSEM images of ZrO_2 xerogels, containing the CoT(p-COOH)PP compound bonded to the pore network, displays a smooth surface without profound cracks or prominent cavities (Fig. 12). EDS mapping indicates homogeneous distributions of Zr, O, and C; the weight % of these elements corresponded to 20.39, 53.12, and 25.05, respectively. As it was mentioned above, the high oxygen percent can be attributed to the formation of a ZrO_2 matrix in which not all oxygen atoms are linked to two zirconium atoms. These oxygens remain in the ZrO_2 network as chemisorbed water or as Zr-OH groups. On the other hand, the sample entrapping the CoT(p-COOH)PP species contains a 4 wt.% more of carbon than samples encapsulating the MTSPc species. This carbon excess can be attributed to the presence of porphyrin macrocycles ($\text{H}_2\text{T(p-COOH)PP} = \text{C}_{48}\text{H}_{30}\text{N}_4\text{O}_8$), especially because of the propylamide bridges ($-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{NH}-\text{CO}-$) that bond these molecules to the pore network (Fig. 2) and, also due to the presence of remnant *acetylacetone* and *propoxyde* groups.

Fig. 12. HRSEM image of a ZrO₂ xerogel with CoT(p-COOH)PP species trapped inside the pores and treated at 225 °C.

The N₂ sorption isotherm at 76 K related to the sample containing cobalt porphyrin macrocycles bonded to the ZrO₂ pore network (Fig. 13a) corresponds to an IUPAC Type IV shape depicting a H4 hysteresis cycle. These characteristics are proper of mesoporous solids in which the pore morphology can be associated to globular aggregates of particles. The NLDFT average pore diameter (Φ) determined from the N₂ desorption experiments (while assuming spherical pore cavities) was 3.4 nm and the specific BET surface area corresponded to 23.2 m²/g. This last value contrasted with the 553.8 m²/g value determined for the analogous silica system [32]; nevertheless, surface areas of around 100 m²/g are still typical of mesoporous ZrO₂ samples. However, with respect to silica xerogels encapsulating CoT(p-COOH)PP species covalently bonded to the pore network, the average pore width was 3.1 nm [44, 45]; *i.e.*, a quantity that is very similar to the value determined for ZrO₂ xerogels. This similitude results obvious, if considering that the distance between the two opposite silicon atoms ($d_{\text{Si-Si}}$) in the CoP-F precursor, ranges from 3 to 3.25 nm (Fig. 2 and 13b). This result confirms that both SiO₂ and ZrO₂ networks are grown around the hydrolyzed silicon or zirconium atoms attached to the precursory molecule. In other words, the size

of the pore cavity that is formed around the solvated precursory molecule depends on its own size. The approach employed to calculate pore widths assumed spherical cavities; therefore, the above results suggest that the interactions between the trapped macrocycle and the pore wall groups take place at both sides of the molecular plane of the trapped species thus, inducing the formation of ellipsoidal rather than spherical cavities (Fig. 13b).

Fig 13. (a) N_2 adsorption-desorption isotherm obtained after thermal treatment at 225°C of a ZrO_2 xerogel containing $\text{CoT}(\text{p-COOH})\text{PP}$ species covalently bonded to the pore network. (b) The dimension of the ZrO_2 (or SiO_2) cavities formed depend of the precursory species CoP-F . In this figure, $d_{\text{Si-Si}}$ represents the separation between opposite silicon atoms attached to the porphyrin molecule and which arises from APTES.

Conclusions

The aluminium tetrasulfo-phthalocyanine, $(\text{OH})\text{AlTSPc}$, was used as a probe to find that molar ratios of $\text{Zr}(\text{OPr}^n)_4$: H_2O : HOPr^n : acac , equivalent to 2: 4: 8: 1, render translucent, monolithic ZrO_2 xerogels. Addition of DMF in that mixture is required to obtain more rigid (i.e. non brittle) samples with the macrocyclic species trapped in monomeric and stable form.

Using that molar mixture it was possible to trap other metallic tetrasulphophthalocyanines, MTSPc ($\text{M} = \text{Fe}, \text{Co}, \text{Ni}, \text{Al}$ and Cu) inside ZrO_2 pore networks. An important result was that the CuTSPc complex, a species endowed with high tendency to form aggregates, remained trapped in monomeric and stable form inside the ZrO_2 pores. This result and together with near infrared analysis showed a weak hydrophilic character, as well as the existence of a smaller amount of ZrOH surface groups in contrast to what happens in SiO_2 xerogel trapping systems. The same methodology was successfully

applied to covalently bonding the CoT(p-COOH)PP compound to the pore walls of ZrO₂, through the bridging action of amine functionalized silicon alkoxides. The average pore widths determined for these samples were very similar to those found for analogue silica systems, indicating that the pore cavity created around of the macrocycle species depends on the own size of this molecule.

The results here obtained presented demonstrate that is possible to successfully trapping synthetic tetrapyrrole macrocyclic species, such as phthalocyanines, porphyrins, or parent natural species such as *chlorophyll* and blood *heme* group, inside the pores of ZrO₂ networks. Through the developed methodology the transcendental physicochemical properties that tetrapyrrole macrocycles display in solution can be even better displayed or tuned up inside new hybrid solid systems, which could be fruitfully exploited in diverse technological fields.

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