Self-organization of porphyrin units induced by magnetic field during sol–gel polymerization†

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The use of a magnetic field as a controlling factor during the hydrolysis–polycondensation of porphyrin precursors substituted by $Si(OR)_3$ groups, induces a self-organization of porphyrin moieties due to the stacking of these units in the hybrid material and this study also confirms the effect of the magnetic field in the nano- and micrometric organization during the kinetically controlled polycondensation process.

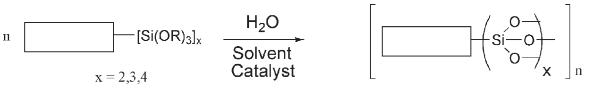
The organization of the organic spacers inside of the matrices of hybrid organic–inorganic materials obtained by sol–gel polymerization[1] has been evidenced recently in the case of precursors containing two, three or even four $Si(OR)_3$ groups (Scheme 1).[2–4]

It has been shown that these processes are under kinetic control.[5] Both van der Waals and hydrogen bonding interactions between hydrophobic units involved during polycondensation at silicon induce self organization of the organic units in the solid.[5]

These materials can be viewed as amorphous since X-ray powder diffraction diagrams exhibit no Bragg peaks. In fact these are non-crystalline organized materials because all the previous organic units incorporated in the framework and studied until now, whatever their geometry – linear rigid, linear with some flexibility, twisted linear, planar, tetrahedral – and the experimental conditions,[5] exhibit X-ray diffraction diagrams showing broad signals consistent with nanometric scale ordering. Unquestionable existence of organization at the micrometric scale has been revealed by birefringence in thin films of the materials.[3c]

These two types of organization appear during two different steps of the process: the nanometric one occurs during the polymerization in solution, whereas the micrometric one takes place in solid phase during the ageing step.[5]

In the present paper we describe the self-organization of bridged organosilica precursors with porphyrin groups. It has been reported that hybrid silica–porphyrin networks can be achieved by sol–gel process,[6] and that these "metalloporphyrinosilicas" containing iron(III) porphyrins for example, catalyze oxidation reactions.[6a] Other applications in sensors,[7] nonlinear optics[8] and hole-burning[9] have also been studied for metalloporphyrins immobilized in sol–gel matrices. More recently supramolecular architectures have been reported in the case of porphyrin precursors presenting cooperative effect of hydrogen bonding and π–π stacking interactions leading to their immobilization in new organic–inorganic hybrid materials.[10]

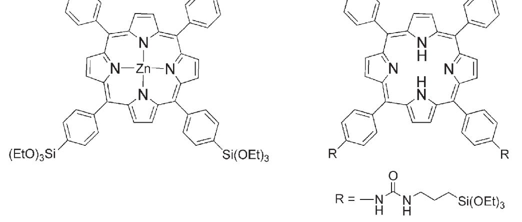


Scheme 1 Sol–gel process of nanostructured hybrid organic–inorganic materials.

In this paper we describe the effect of magnetic field as a controlling factor for the self-organization of porphyrin moieties in organic inorganic material prepared by hydrolytic polycondensation (sol–gel route). Two porphyrin precursors with completely different structures were investigated. 5,10,15,20-Tetrakis[4-(triethoxysilyl)phenyl]porphyrin zinc **P1** presents a rigid zinc porphyrin metallated core and the free base 5,10,15,20-tetrakis[4-(3-triethoxysilyl)propylureido)phenyl]porphyrin **P2** possesses flexible arms containing ureido groups favoring H-bonds (Scheme 2). The hydrolytic polycondensation was performed with (xerogels **X1M** and **X2M** for **P1** and **P2**, respectively) and without magnetic field (xerogels **X1** and **X2** for **P1** and **P2**, respectively).

The tetraethoxysilyl metalloporphyrin **P1** was prepared as described below. 5,10,15,20-Tetrakis(4-bromophenyl)porphyrin was synthesized following the Adler–Longo procedure and the metalation was done as reported in the literature.[11] Silylation[12] was performed by using triethoxysilane in the presence of NEt_3 and a catalytic amount of $[Rh(cod)(MeCN)_2]BF_4$. **P1** was obtained as a purple solid in 65% yield. The tetraethoxy-ureido porphyrin **P2** was synthesized by condensing four 3-(triethoxysilyl)propyl isocyanate with the amino functions of the 5,10,15,20-tetrakis(4-aminophenyl)porphyrin in the presence of triethylamine.[13] The free base amino porphyrin was obtained by reducing the tetranitro derivative in the presence of $SnCl_2 \cdot 2H_2O$.[14]

The corresponding bridged porphyrylpolysilsesquioxanes **X1**, **X2**, **X1M** and **X2M** were prepared by hydrolysis–polycondensation of the precursors in THF for **P1** and in DMSO for **P2** due to



Scheme 2 Tetraethoxysilyl porphyrins **P1** and **P2**.

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Table 1 Properties of the xerogels

Precursor	Xerogel	Conc./mol L^{-1}	t_{gel}/min	S_{BET}/m^2 g^{-1}	^{29}Si CP MAS NMR (%) T^0	T^1	T^2	T^3	L.C.^{a} (%)	Birefringence ($\times 10^3$)
P1	**X1**	0.05	1920	280	0	11	45	44	78	4.7
P1	**X1M**^{b}	0.05	1920	447	0	13	43	44	77	5.8
P2	**X2**	0.1	54	<10	0	30	50	20	70	7.7
P2	**X2M**^{b}	0.1	30	<10	0	0	39	61	87	8.4

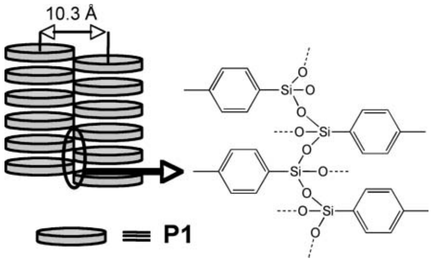
^{a} Degree of condensation calculated according to the general equation L.C. = [0.5 (T^1 area) + 1.0 (T^2 area) + 1.5 (T^3 area)]/1.5. ^{b} Under magnetic field (4.7 Tesla)

the very low solubility of **P2** in THF, at room temperature in the presence of 2% mol of tetrabutylammonium fluoride as catalyst (TBAF). The xerogels **X1M** and **X2M** were prepared in a magnetic field of 4.7 Tesla‡ at room temperature. The gels are formed after various gelation times and the resulting solids were treated as usual.[5] The xerogels were isolated as dark purple solids in almost quantitative yield (calculation based on a fully polycondensed solid, 96–98%). The experimental conditions, specific surface areas, spectroscopic data and birefringence values for these solids are given in Table 1.

In the case of **X1M** and **X1**, the ^{29}Si CP MAS NMR spectra displayed three resonances at ~-70, ~-80 and ~-89 ppm, assigned, respectively, to T^1, T^2 and T^3 substructures. The level of condensation, estimated in first approximation by deconvolution of spectra,[15] was observed in the same range (70–80%) (Table 1). In the case of **X2**, three resonances at ~-49, ~-58 and ~-65 ppm (T^1, T^2 and T^3) were observed while for **X2M** the spectra exhibited only two signals at ~-59 and ~-64 ppm. The level of condensation was higher when the gel was performed under magnetic field (87% *versus* 70%). The electronic spectra in the diffuse reflectance mode were performed by dispersing the xerogels in silica. The presence of a band in the Soret region (λ_{max}/nm: 422 for **X1**, 421 for **X1M**) and two Q bands (λ_{max}/nm: 558 and 602 for **X1**, 560 and 603 for **X1M**) for each gel indicates that the porphyrin rings were not modified during the hydrolysis-polycondensation process.

As already described for all nanostructured hybrid materials reported until now,[5] the X-ray diffraction diagrams of **X1**, **X2**, **X1M** and **X2M** did not exhibit sharp Bragg signals (Fig. 1), but broad and intense signals were observed. It is well established that these broad signals correspond without any doubt to the existence of a nanometric scale level in the material.[16] Assuming Bragg's law, the distances associated to the *q* values were calculated ($d = 2\pi/q$).

The shape of the X-ray diffraction diagrams (from 0.2 to 2.0 Å^{-1}) was the same for all the solids prepared from **P1** whatever the experimental conditions: two broad signals were observed at $\sim$0.61–0.63 Å^{-1} (10.0–10.3 Å) and a weak one at $\sim$1.57–1.61 Å^{-1} (3.9–4 Å). Considering a columnar stacking of the macrocycles, the first signal has been attributed to the distance between two columns, the medium planes being defined by the zinc atoms presenting the higher electron density (Scheme 3). The weaker signal is attributable to the Si–O–Si units contribution.[16]



Scheme 3

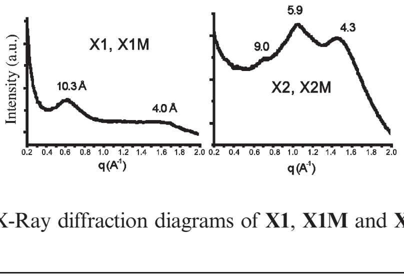


Fig. 1 X-Ray diffraction diagrams of **X1**, **X1M** and **X2**, **X2M**.

In the case of the solids obtained from **P2**, three broad signals were observed at 9.0, 5.9, and 4.3 Å. This behavior is similar to that of other polysilsesquioxane materials prepared from precursors possessing H-bond interactions.[17] It was difficult in this case to assign the distances of 9.0 and 5.9 Å.

More information has been obtained between 0.04 and 0.24 Å^{-1} by SAXS experiments (Fig. 2). A diffraction signal was observed in this area only in the case of the xerogels **X1M** and **X2M** prepared under magnetic field, at 0.12 Å^{-1} (52.3 Å) for **X1M** and at 0.077 Å^{-1} (81.9 Å) for **X2M**, whereas without magnetic field (case of **X1** and **X2**), no signal was observed. Taking into account a distance of around 3.5 Å between a zinc atom and the medium plane of the next porphyrin unit,[18] the distance of 52.3 Å in the case of **X1M** can correspond to a stacking of 15 units. In the case of **X2M**, the intensity of the signal observed at 81.9 Å is higher and the signal is more narrow. This is indicative of a better organization in the solid as expected because of hydrogen bonding. This distance can correspond to the stacking of 23 units.

Such a behavior can be explained from the strong interaction between the applied magnetic field and the diamagnetism induced by the 18 π electrons of the macrocycle (Scheme 4). Thus all the molecules should be forced to orient and organize one to each other in the direction of the magnetic field lowering the entropy of the polycondensation reaction and leading to the stacking of porphyrin rings as shown in Scheme 4.

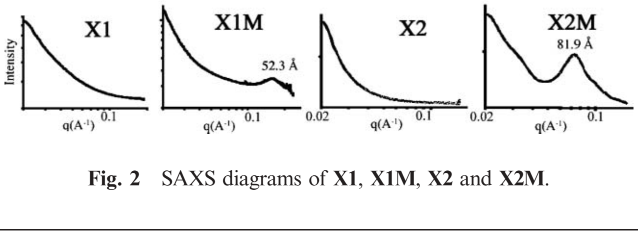
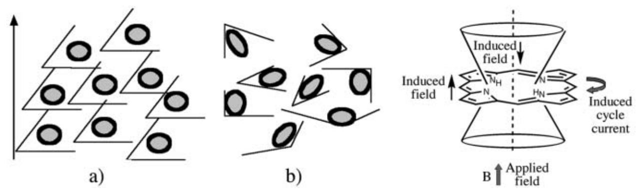


Fig. 2 SAXS diagrams of **X1**, **X1M**, **X2** and **X2M**.



Scheme 4 Schematic comparison of the orientation of porphyrin units: (a) in a magnetic field, (b) without magnetic field; and (c) interaction between the magnetic field and the macrocycles.

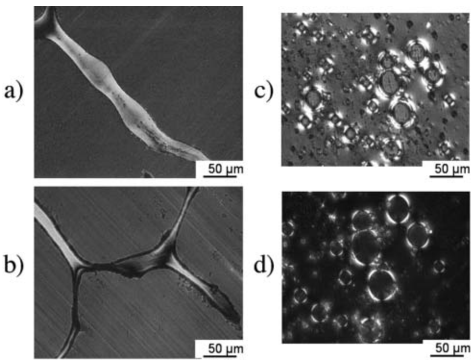


Fig. 3 Birefringence pictures of (a) **X1**, (b) **X1M**, (c) **X2**, (d) **X2M**.

The sol, initially placed in a magnetic field, was taken up a few minutes before the gel point and introduced by capillarity in a thin Teflon-coated cell which was then sealed and placed in the magnetic field. The sol–gel transition was observed in the cell after 15 min. The same experiment was performed to afford the xerogels **X1** and **X2**, but without applying a magnetic field. Both cells were analyzed by microscopy in polarized light. An important shrinkage and the formation of birefringent purple wires of gel without cracks were observed in the case of **P1**. The same morphology was observed for the gels **X1** and **X1M** (Fig. 3).

Teflon coating between the gel wires was observed. The important shrinkage is a priory due to the low concentration of the precursor. The birefringence intensity was slightly higher under magnetic field (4.7×10^{-3} for **X1** and 5.8×10^{-3} for **X1M**) and the optical axis was oriented, as usual, perpendicularly to the axis of the wires in both cases (Fig. 3). Furthermore, it is well known that porphyrins, and especially rigid ones, tend to align according one-dimensional aggregates,[10] therefore the fiber-like morphology observed for the gels **X1** and **X1M** could depend on the architecture of the precursor.

In the case of **X2** and **X2M**, both gels exhibited the same morphology, very different of that of the gels **X1** and **X1M** (Fig. 3(c) and (d)). Such morphology has been already observed in the case of gels obtained from TTF or planar precursors having flexible arms.[18]

The results presented here show clearly the drastic effect of the magnetic field in the self-organization of the porphyrin units during the polycondensation process. This effect is mainly observed at the nanometric scale level, since the SAXS diagram is totally different when a magnetic field is applied during the gelation process. In contrast the micrometric scale organization is the same in both cases (similar birefringence phenomena and orientation of optical axis). Thus these results confirm unambiguously that the nanometric and the micrometric scale organizations take place during different steps of the polycondensation process and are not governed by the same parameters.§

Notes and references

‡ The intensity of the field was measured with a teslameter. The sample was displayed under the magnet of a 250 MHz NMR Brüker apparatus, near the probe using a wood made device.

§ *Synthesis* of the xerogels: The preparation of the xerogels was carried out according to a general procedure. The preparation of **X1** is given as an example: 0.34 g (0.25 mmol) of **P1** and 1.27 mL of dried THF were introduced in a Schlenk tube. 1.27 mL of a solution containing 2.5 µL (2.5 µmol) of TBAF (1 mol L^{-1} in THF), 27 µl (1.52 mmol) of H_2O and 1.24 mL of dried THF, were added. This mixture was introduced by capillarity into the observation cell just before the gel point, and the remaining solution was kept in the Schlenk tube. In both cases, after the sol–gel transition, the dark gel was aged 6 days. Then, the gel obtained in the Schlenk tube was crushed and washed twice with acetone, ethanol and diethyl ether, and the resulting powder was dried at 120 °C under vacuum for 3 h yielding a dark purple xerogel. In the case of **X1M** or **X2M**, the process was performed in a magnetic field of 4.7 Tesla.

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