

Direct synthesis of Mesoporous Hybrid Organic-Inorganic Silica Powders and Thin Films for Potential Non Linear Optic Applications

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Abstract Powders of mesoporous organosilica functionalized with a Non Linear Optical chromophore in the channel pore (azobenzene diethylphosphonate) were achieved in one step and were synthesized by templated-directed co-condensation of tetraethylorthosilicate (TEOS) and the functional organotriethoxysilanes. The materials were characterized by ^{13}C , ^{31}P and ^{29}Si NMR experiments, nitrogen gas adsorption, powder X-ray diffraction (XRD). Optically transparent and highly ordered multifunctional mesostructured films obtained by evaporation induced self-assembly (EISA approach) approach were deposited on glass or silicon substrates by dip-coating. Thin films were monofunctionalized in the channel pores or bifunctionalized (channel pore/framework) and allowed us to evidence the salt effect induced by an organometallic complex on the structure of the mesostructured film. They were characterized by Grazing Incidence Small Angle X-ray Scattering (GISAXS) and X-ray reflectivity.

Keywords Hybrid materials · NLO · bifunctionality · thin films · mesoporous and GISAXS

The study of functionalized hybrid organic–inorganic materials is an expanding field of investigation, which should give rise to advanced materials [1].

Ordered mesoporous silicas are of particular interest for several applications, because of highly uniform porosity, mechanical stiffness, and thermal stability.

Such materials have often been prepared by post-synthetic grafting of an organotrialkoxysilane, $\text{RSi}(\text{OR}')_3$, onto the pore surface of ordered mesoporous silica [2–5].

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This post-synthetic process has allowed the anchoring of a large number of organic groups, including bulky ones. However, this method does not allow to control the loading or the distribution of the functional groups on the inner pore surfaces [6, 7]. One alternative approach consisted of the introduction of organic groups during the synthesis of the material by the co-condensation of tetraethylorthosilicate (TEOS) and an organotriethoxysilane $\text{RSi}(\text{OEt})_3$ in the presence of a structure-directing agent. In this case, the functional groups of the resulting materials are regularly distributed on the pore surfaces [8].

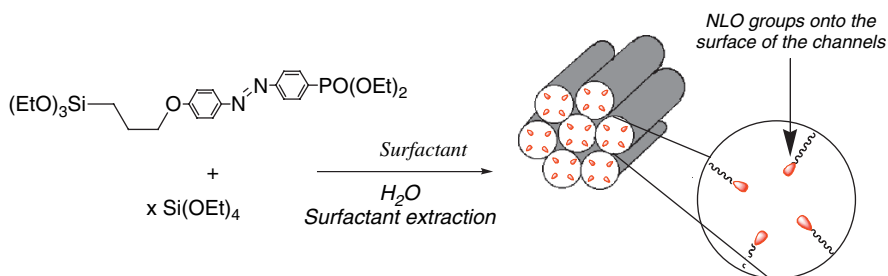
A variety of shapes, including thin films and monoliths, can be prepared, exhibiting good optical properties (transmission in visible range) and mechanical strength (easy machining) required for optical properties [9]. Then, numerous silica and siloxane-based hybrid organic–inorganic materials, mainly as coatings, have been developed in the past years, showing emission (solid-state dye lasers, electroluminescent devices), photochromism (optical switching, information storage), optical non linearity (second-order NLO, hole-burning) and sensing properties [10, 11].

As silica is transparent in the UV-visible range, these materials are ideal for optical applications. The mild synthesis conditions offered by the sol–gel process allow the incorporation of optically active organic molecules into the glassy matrix to form doped gels with specific optical properties.

Second-order non-linear optics continue to be an area of research because of its tremendous potential in the design of photon-based new materials for optical switching, data manipulation, and information processing [12].

Optimized NLO chromophores were incorporated into organic-inorganic hybrid materials through sol-gel process [7, 13]. This class of hybrid materials is very competitive for photonic application due to its peculiar properties, such as high transparency, low optical propagation losses and easy film processing. Such system containing covalent bonds between NLO chromophores and the host matrix network represents an interesting alternative to organic polymers, which exhibit poor reproducibility of optical quality and low T_g .

We now describe the synthesis of a mesoporous hybrid material containing silylated azobenzenediethylphosphonate ligand located in the channel pores, by hydrolytic polycondensation of the compound **1** (Scheme 1) in the presence

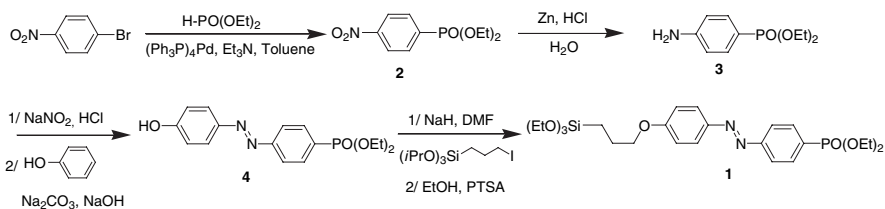


Scheme 1 General pathway for the preparation of mesoporous bifunctionalized organo-silica thin films (See also Plate 16 in the Colour Plate Section)

of a structure-directing agent. The presence of chelating function on the NLO chromophore is expected to raise the NLO response by complexing a salt or coupling different properties as NLO and photoluminescence with a lanthanide salt.

As powders are unfavorable with respect to the potential applications in nonlinear optics and in the optical characterization of the composites, ordered mono and bifunctionalized organo-silica thin films were prepared through evaporation-induced self-assembly (EISA) and characterized.

The synthesis of the mono-silylated azobenzene diethylphosphonate **1** is outlined in Scheme 2: the 4-nitrophenyldiethylphosphonate **2** was synthesized thanks to a palladium catalyzed P–C cross coupling between diethylphosphonic acid and 4-bromonitrobenzene. This procedure [14] afforded **2** in 80% yield after purification. In order to perform the diazocoupling, nitro function of **2** was reduced by a Clemmensen type procedure to obtain **3** in a quantitative yield without further purification. The 4-(4-hydroxyphenylazo)phenyldiethylphosphonate **4** was synthesized by the diazocoupling reaction between **3** and the phenol. The silylation of **4** was accomplished by a Williamson type reaction with iodopropyl triisopropoxy-silane. It is worth noting that triisopropoxy groups were preferred to triethoxysilyl groups in silylation reactions, because the isopropoxy groups are poorly reactive especially towards hydrolysis. That allowed the purification by silica column chromatography in 71% yield. Finally, isopropoxide/ethoxide exchange was achieved in ethanol in presence of p-toluene sulfonic acid as catalyst to give compound **1** in high yield (Scheme 2). The organosilane **1** was fully characterized by ^1H , ^{31}P , ^{29}Si , ^{13}C NMR spectroscopies, and elemental analysis.



Scheme 2 Sequence of reaction for the preparation of the precursor **1**

The functional materials of **SBA-15** type were prepared by co-hydrolysis and polycondensation of **1** and x equivalents of tetraethylorthosilicate (TEOS) in presence of P123 as structure directing agent. The materials obtained were called **SBA1a** and **1b** for $x=9$ and 19 respectively. Our procedure was the following:

1.46 g of P123 was dissolved in 58 mL of a mixture ethanol/aqueous HCl solution pH=1.5 (75/25 v). This solution was added to a mixture of 3.1 g of TEOS ($x=9$) and 0.9 g of **1** at ambient temperature. The mixture was stirred for 3 h giving rise to a micro-emulsion. After heating this perfectly transparent solution at 60°C, a small amount of NaF (30.0 mg) was added with stirring to induce the polycondensation. The mixture was stirred at 60°C for 48 h. The resulting solid was filtered off and washed. The surfactant was then removed by hot ethanol extraction in a Soxhlet

apparatus affording 1.5 g of the **SBA1a** as an orange powder in 88% yield. The molar composition of the reaction mixture was: 0.04 F⁻: 1 TEOS: 0.11 **1**: 0.02 P123: 0.03 HCl: 54 H₂O: 50 EtOH.

Small-angle X-ray scattering patterns exhibit a weak single diffraction peak at $q=0.68$ and 0.66 nm^{-1} for **SBA1a** and **SBA1b** respectively, characteristic of the wormlike structure (Fig. 1) with a regular pore-pore distance [15]. The corresponding d value was calculated to be 9.2 and 9.5 nm respectively.

The N₂ adsorption-desorption measurements (Fig. 2) showed a type IV isotherm, characteristic of mesoporous materials with BET surface areas of 303 and 608 m².g⁻¹ for **SBA1a** and **SBA1b** respectively, and narrow pore size distributions centered at 3.7 and 5.9 nm.

The incorporation of **1** in the mesoporous materials and the removal of surfactant were shown by solid-state NMR spectroscopies. ¹³C CP-MAS NMR spectrum of **SBA1a** (Fig. 3) exhibits two signals at 63.13 (CH₂-O) and 15.94 ppm (CH₃-CH₂), revealing the presence of diethylphosphonate groups. The spectrum exhibits three additional signals attributed to the propyl spacers at 69.86 (CH₂O), 22.89 (CH₂), and 7.99 ppm (CH₂Si). Seven signals in the aromatic area were characteristic of diazodiphenyl unit.

Solid-state ²⁹Si CP-MAS NMR spectrum of **SBA1a** displayed signals at -101.32 and -110.07 ppm attributed to the substructures Q³ and Q⁴, respectively, denoting high cross-linking of the silica. One additional peak at -66.58 ppm assigned to the substructure T³ [C-Si(OSi)₃], indicates the high cross-linking of the organosilsesquioxane species.

The solid state ³¹P NMR spectrum of **SBA1a** and **SBA1b** displays one signal at 19.20 ppm proving that the diethylphosphonate groups were not modified during the sol-gel process.

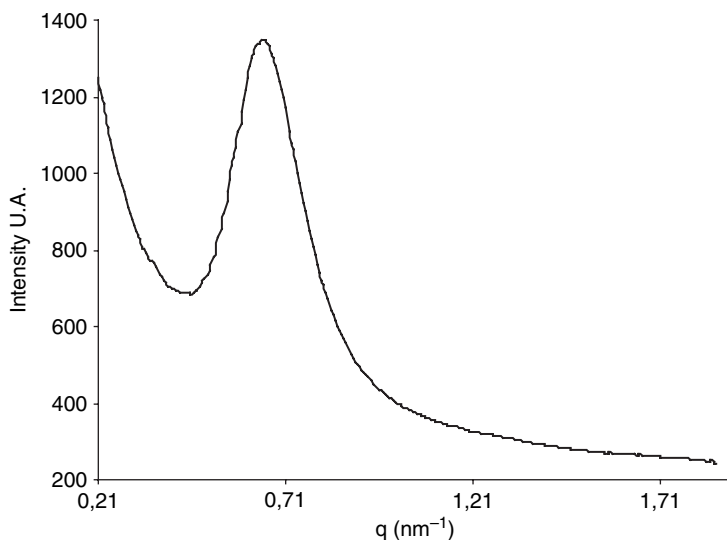


Fig. 1 SAXS pattern of **SBA1b**

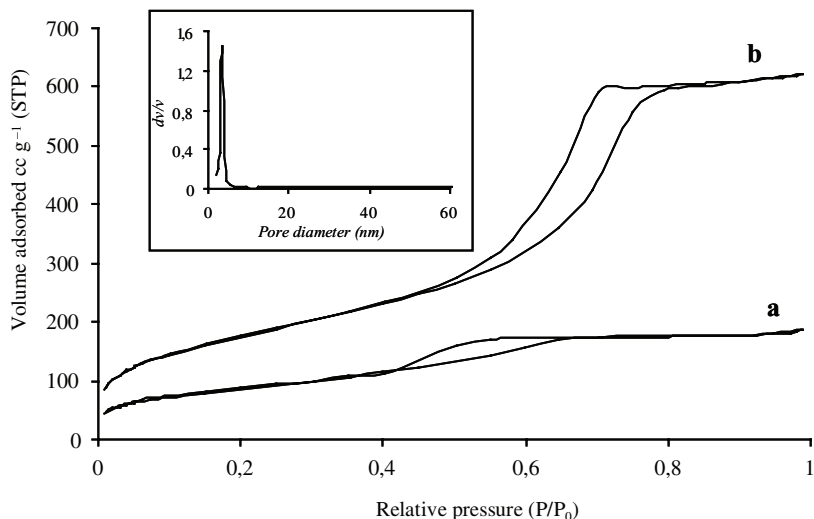


Fig. 2 N₂ adsorption-desorption isotherm of **SBA1a** (a) and **SBA1b** (b). The inset shows the BJH pore size distribution plot for **SBA1a**.

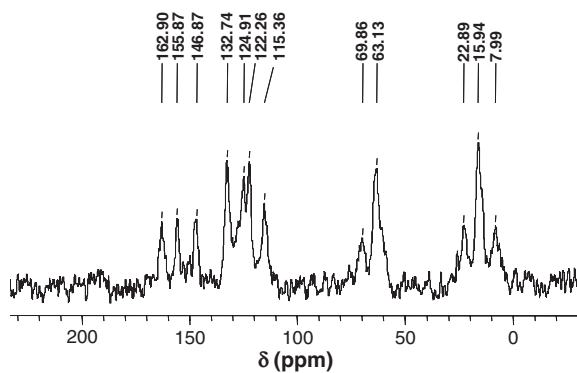


Fig. 3 ¹³C CP/MAS NMR spectrum of **SBA1a**

The results of the elemental analysis of the final material led to the experimental formula C₁₉H₂₉N₂PSi₁₀, the calculated formula being C₁₉H₂₄N₂PSi₁₀, which indicates that the loading in azobenzene diethylphosphonate is close to the expected value.

A standard procedure [16] was adapted for the preparation of functional ordered organosilica thin films. The initial sol was prepared in two times. First, a pre-hydrolysed hybrid sol was prepared by mixing 1.66 g of TEOS (7.98 mmoles), 0.23 g (0.42 mmoles) of **1**, 1.0 g of ethanol and 1.25 g of H₂O (pH=1.5). The resulting mixture was stirred at room temperature for 1h. A second solution containing 0.6 g of P123 and 27.2 g of EtOH was then added to the sol. After 2 h of stirring, 2.0 g of H₂O (pH=1.5) was added. Thin films were then prepared by dip-coating float glass substrates in the solution at a constant withdrawal speed of 14 cm *per* minute in a sealed cabinet in which the relative humidity

was maintained at 70% and the temperature at 25°C. The resulting thin film called F_{SBA1b} was obtained after 10 min of aging time under the same conditions. The surfactant template was selectively removed by solvent extraction using Soxhlet apparatus and EtOH under reflux for 6 h.

The structure of the thin films was characterized by both GISAXS measurements and X-ray reflectivity (XRR). GISAXS measurements were carried out at Brookhaven National Laboratory at the X22B beam line of the NSLS. The incident beam had a fixed energy, $E=8$ keV. It was impinging on the surface of the sample at an angle of incidence of about 0.25° (slightly above the critical angle of incidence of the glass substrate) to fully penetrate inside the thin film. The GISAXS patterns were collected on a MARCCD detector located 73 cm after the sample and the specularly reflected beam was attenuated with a beam stop to avoid detector saturation. XRR measurements were performed on the Philips reflectometer of LPEC laboratory (Université du Maine, Le Mans). The X-ray beam coming out of a copper tube was monochromatized with a 0002 graphite monochromator.

Figure 4b shows the GISAXS pattern measured after surfactant extraction. Surprisingly, it can be seen that the pattern exhibits a lamellar symmetry.

The XRR (Fig. 4.a) shows the scattering features along the specular direction with a dynamical range of more than six orders of magnitude. All the films exhibit Bragg reflections located at almost the same wave vector transfer. A rough estimation from the Bragg peak positions yields $d_{100}=4.8$ nm and $d_{200}=2.4$ nm confirming the lamellar structure while the bulk material was not organized.

Then, we attempted to prepare a 2D hexagonal mesoporous organosilica thin film containing **1** in the channel pores and an erbium complex **5Er** (the synthesis of which was previously described [17]) in the framework (Scheme 3).

Indeed, inorganic salts have been used to improve the hydrothermal stability [18–20], control the morphology [21–23], extend the synthesis domain [24], and tailor the framework porosity [25, 26] during the formation of mesoporous

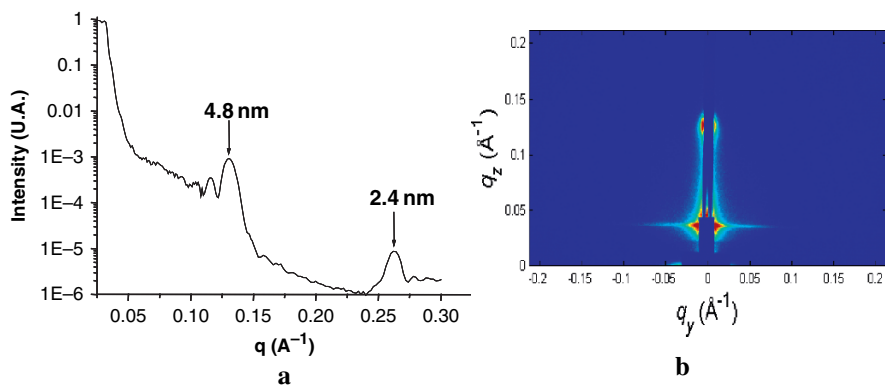
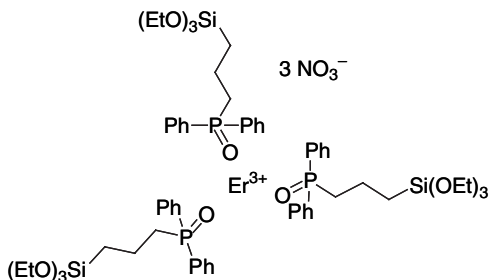


Fig. 4 X-ray reflectivity curve (a) and GISAXS pattern (b) showing the lamellar structure of the film F_{SBA1b}

Scheme 3 Erbium complex **5Er** introduced in the framework



materials. Our goal was to combine the inorganic salt effect and the control of the structure of the organosilica in order to obtain a bifunctional (channel pore/framework) mesoporous organosilica thin films. The thin film named $F_{SBA1,5Er}$ was prepared from precursors **1** and **5** according to the same procedure as this used for F_{SBA1b} .

Figure 5b shows the GISAXS pattern of $F_{SBA1,5Er}$ measured after surfactant extraction. It can be seen that this pattern exhibits the 2D hexagonal symmetry characteristic of the $p6m$ space group. The XRR (Figure 5.a) shows the scattering features. A rough estimation from the Bragg peak positions yields $d_{10} = 6.5$ nm and $d_{20} = 3.4$ nm confirming the 2D hexagonal structure.

These results can be attributed to the specific effect of the erbium salt on the self-assembly interaction between surfactant head-groups and inorganic species [27].

In non-ionic surfactant templating systems, the effect of ionic strength has also been studied [28, 29]. Generally, ionic interactions are emphasized in these reports, which leads to better order either in mesostructure or morphology [30]. In our case, we obtained the same result, but this is the first time to our knowledge, that an organometallic complex acts as an inorganic salt in the structuration of an organosilica.

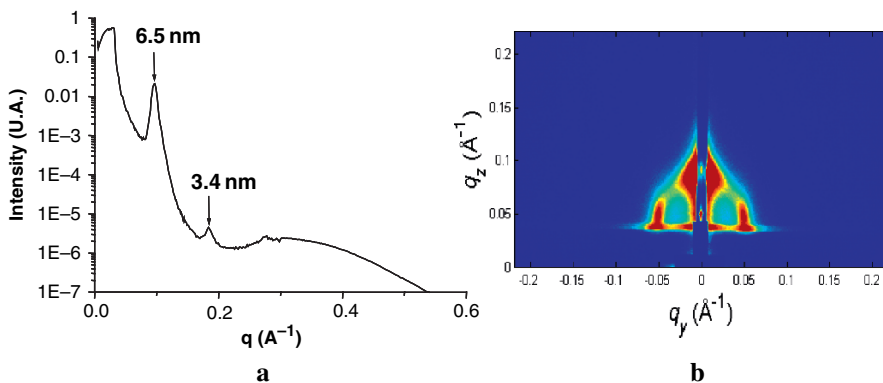


Fig. 5 X-ray reflectivity curve (a) and GISAXS pattern (b) showing the 2D-hexagonal structure of the film $F_{SBA1,5Er}$

In conclusion, we first described the one step synthesis of nanoporous organosilica powders functionalized with a Non Linear Optical chromophore in the channel pore (azobenzene diethylphosphonate). These powders have been totally characterized and present a meso-porosity with a wormlike structure. Thin films monofunctionalised with NLO chromophore in the channel pores or bifunctionalized (NLO in the channel pores/erbium salt in the framework) were also prepared in one step and characterized by Grazing Incidence Small angle X-ray Scattering (GISAXS) and X-ray reflectivity. Interestingly, while the monofunctional thin film F_{SBA1b} presents a lamellar structure, the bifunctional one $F_{\text{SBA1,5}}$ (channel pores/framework) presents a 2D-hexagonal phase having $p6m$ symmetry. Thus, the GISAXS experiments highlighted a salt effect on the final structure of the thin films. This is a clear evidence that a complex could act as an inorganic salt in the structuration of mesoporous films. Further investigations coupling other functional organic groups and complexes are now in progress in order to attempt a generalization of this effect. Our synthetic approach is a route to produce interactive materials in thin films, i.e. materials simultaneously coupling two properties at the nanometric scale.

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