One-step template-directed synthesis of multifunctionalised nanoporous silica: on the way to interactive nanomaterials†

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The preparation of multifunctional mesoporous silica containing a NLO chromophore in the framework (bridged azobenzene phosphonium salts) and mercaptopropyl groups able to stabilize gold(0) nanoparticles in the channel pores was achieved in one step by using the direct liquid crystal templating approach.

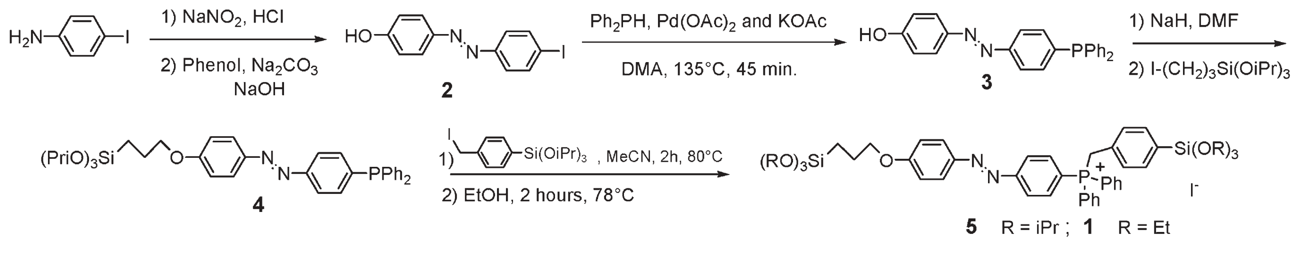
The recent use of bridged silsesquioxanes $[(R'O)_3Si]_mR$ ($m \geqslant 2$), as precursors for periodic mesoporous organosilicas (PMOs) prepared in the presence of structure-directing agent was a remarkable advance in material science.[1–4] This novel route gives rise to materials, which cannot be obtained by other approaches.[5] Indeed, the organic moieties are homogeneously integrated to the silicate framework leaving the channel pores unoccupied. This last point is of great interest because it thus opens the route to interactive nanomaterials in which two physical properties can be introduced, one in the channel pores and the other in the framework. These two properties located at a nanometric range to each other are susceptible to present unexpected interactions.

Though this concept has been caught as early as the discovery of PMOs, the introduction in the framework of only rather small bridging aliphatic or aromatic moieties, relatively inert chemically is well controlled, either with terminal organic functional groups in the channel pores[6–8] or not.[5] Thus, the next step is the discovery of chemical methods, which permit the introduction within the walls of large, and eventually flexible functional organic groups, generating frameworks with chemical or physical properties. The limiting factors for this purpose arise from the lack of available precursors with the required rigidity for structure formation. Mesoporous hybrid materials containing chiral groups[9] or strongly chelated transition ions[10] in the framework are the more representative examples on the way to such materials. We previously succeeded in preparing mesoporous hybrid materials containing two strongly chelated metal ions, one in the framework, and the other in the pore channels. However, because of the flexibility of the chelating units (cyclam moieties), we did not obtain ordered pore structure.[11]

In this paper, we report a one-step procedure which allows introducing a rather large NLO chromophore in the framework and mercaptopropyl groups in the channel pores of mesoporous silica by using the direct liquid crystal templating approach.[10] Gold(0) nanoparticles were successfully stabilized by mercapto groups located within the channels of the multifunctional mesoporous material.

The choice of the bis-silylated azobenzene phosphonium salt chromophore **1** (Scheme 1) containing an ether donor group and an ionic phosphonium acceptor group was inspired from a non silylated phosphonium salt, which was proved to be a very efficient NLO chromophore.[12] On the other hand, the mercaptopropyl group was selected for the functionalisation of channel pores because we showed that such functional groups located in the channel pores of ordered mesoporous hybrid materials are very convenient for *in situ* formation of gold(0) nanoparticles.[13] As the presence of gold nanoparticles in a material containing an NLO chromophore is expected to raise the NLO response,[14] it was of interest to locate mercaptopropyl groups in the channel pores of materials containing the NLO chromophore in the framework.

The synthesis of the bis-silylated azobenzene phosphonium salt **1** is outlined in Scheme 1: the 4-(4-iodophenylazo)phenol **2** was synthesized by the diazocoupling reaction between the *p*-iodoaniline and the phenol. The phosphorylation of **2** was achieved thanks to a palladium catalyzed P–C cross coupling between diphenylphosphine and the iodo derivative.[15] This procedure afforded **3** in 80% yield after purification. Bridged silsesquioxane was then achieved in two steps. First, the silylation of **3** giving **4** was accomplished by a Williamson type reaction with iodopropyltriisopropoxysilane. No quaternisation took place during this reaction. 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 of **4** by silica column chromatography in 79% yield. **4**



Scheme 1 Synthesis of bis-silylated azobenzene phosphonium salts **1**.

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† Electronic supplementary information (ESI) available: preparation of material $S_{1,SH}^{Au}$. See http://www.rsc.org/suppdata/cc/b4/b417522k/

was then subsequently quaternised with *p*-iodobenzyltriisopropoxysilane. The bridged silsesquioxane **5** was fully characterized by ^{1}H, ^{31}P, ^{29}Si, ^{13}C NMR spectroscopies, and elemental analysis. Finally, isopropoxide/ethoxide exchange was achieved just before reacting, yielding **1**.

The multifunctional material was prepared by co-hydrolysis and polycondensation of **1**, tetraethylorthosilicate (TEOS) and 3-mercaptopropyltriethoxysilane (MPTE) in lyotropic liquid crystal medium. Indeed, as the bridging organic groups are rather large and flexible, *i.e.* do not present structural rigidity required to order the material, high surfactant concentration of the non ionic triblock copolymers P123 was preferred. Furthermore, such conditions allow obtaining a monolith, which could be an advantage for applications. The procedure was the following: 0.70 g of $EO_{20}PO_{70}EO_{20}$ was dissolved in 1.7 mL of an aqueous HCl solution (pH 1.5). 3.25 g (15.62 mmol) of TEOS was then added. The mixture was stirred until a clear solution was obtained. 0.31 g (1.28 mmol) of MPTE was added and 30 min later, 0.17 g (0.17 mmol) of **1** was put into the clear solution obtained. When the mixture was clear, ethanol was removed under vacuum. The monolith was kept 24 h at room temperature and then hydrothermally treated at 95 °C for 20 h. The solid was recovered by hot ethanol extraction in a Soxhlet apparatus for 24 h, dried and washed as previously described to yield 1.40 g of an orange powder (89% yield), which was called $\boldsymbol{S_{1,SH}}$.

The results of the elemental analysis of the final material led to the experimental formula $PS_{13}Si_{130}I$, the calculated formula being $PS_{9}Si_{101}I$. That indicates that the loading in mercaptopropyl groups (17.8% w) is close to the expected value (16.0% w), while that of the bridged azobenzene phosphonium salt was inferior (8.0% w instead of 10.0). That is probably due to the large size of the phosphonium group. The N_2 adsorption–desorption isotherm of the material (Fig. 1) was of type IV, characteristic of mesoporous materials with a narrow pore size distribution. The S_{BET} was found to be 656 $m^2\ g^{-1}$ and the mean pore diameter ranges from 3.5–5.5 nm.

Small-angle X-ray scattering pattern of $\boldsymbol{S_{1,SH}}$ exhibits a single diffraction peak, characteristic of a wormhole framework with a d_{100} spacing of 9.48 nm. The mean thickness of the pore walls (7.63 nm) was estimated from the d_{100} spacing and the mean pore size. It is worth noting that this value is large compared to the mean thickness of the pore walls for silica containing functional groups only in the channel pores and prepared in the presence of P123 as a template.[16–18] That is a good indication of the location of the bridged azobenzene groups in the framework.

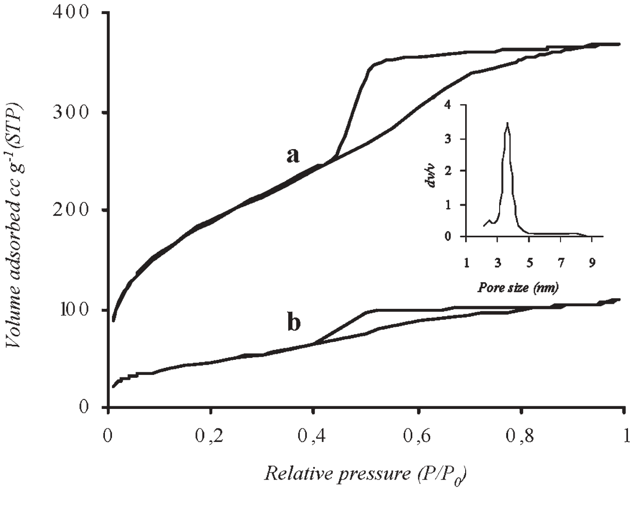

Fig. 1 N_2 adsorption–desorption isotherms of $\boldsymbol{S_{1,SH}}$ (**a**) and $\boldsymbol{S_{1,SH}^{Au}}$ (**b**). The inset shows the BJH pore size distribution plot at desorption of $\boldsymbol{S_{1,SH}}$.

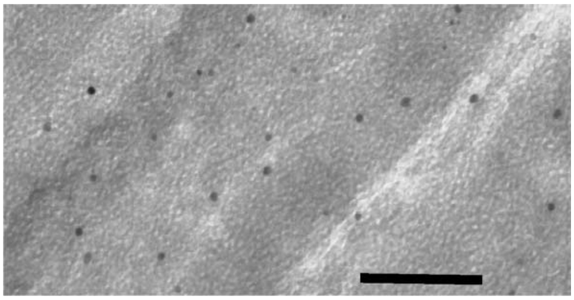

Fig. 2 TEM image of material $\boldsymbol{S_{1,SH}^{Au}}$. Scale bar = 100 nm.

The solid state ^{31}P NMR spectrum of $\boldsymbol{S_{1,SH}}$ displays one signal at 22.48 ppm proving that the phosphonium group was not modified during the sol–gel process. ^{29}Si CP-MAS NMR spectrum exhibits a signal centered at −65.4 ppm, attributed to T^3 resonance in addition to an intense peak at −100.7 ppm and another one at −108.0 ppm, respectively, assigned to Q^3 and Q^4 substructures.

Gold(0) nanoparticles were prepared according to a procedure, which we adjusted previously on SBA-15 type materials containing mercapto groups in the channels pores:[13] $\boldsymbol{S_{1,SH}}$ was first treated with chloro(tetrahydrothiophene)gold(I) AuCl(THT) as organogold precursor with a [Au]/[SH] ratio of 0.05 then with an ethanolic sodium borohydride ($NaBH_4$) solution for 8 h to give an orange–brown solid after filtration and drying (see ESI†). The SAXS pattern of the resulting material $\boldsymbol{S_{1,SH}^{Au}}$ revealed the absence of a diffraction peak, which is an indication of the pore filling of the host material.[13] A notable decrease in BET surface area (Fig. 1) was also observed (S_{BET} = 207 $m^2\ g^{-1}$) confirming the pore filling. Finally the TEM image (see Fig. 2) shows uniformly sized spherical nanoparticles centred at 5.5 ± 1.5 nm in agreement with the pore size range of the host material.

In conclusion, we described a one-step methodology (the direct liquid crystal templating (LCT) approach) allowing a mesoporous silica, containing a NLO chromophore[12] in the framework (bridged azobenzene phosphonium salts) and mercaptopropyl groups able to stabilize gold(0) nanoparticles in the channel pores, to be obtained.[13] This is the first example of ordered mesoporous materials containing a large functional group in the framework, and another in the channel pores prepared in one step thanks to the LCT approach. This methodology could be a general route for such materials coupling two properties, which could interact.[14]

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