

An original synthesis of highly ordered organosilica with a high content of thiol groups†

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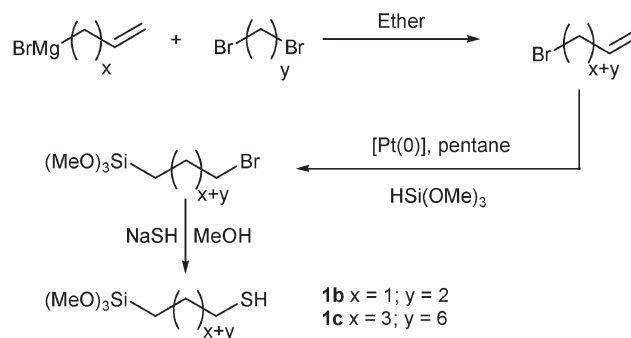
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Well ordered bridged organosilica highly functionalised with disulfide groups were obtained by self-assembly of α, ω -bis(trimethoxysilyl)alkyldisulfide under hydrophilic conditions; the reduction of disulfide cores to SH groups gave rise to material having a high mercury ion adsorption capacity.

Ordered thiol-functionalized hybrid materials^{1–5} have received considerable attention in recent years due to their numerous potential applications for heavy metal ion adsorption,⁶ separations, metallic nanoparticles stabilization⁷ and also in the field of catalysis⁸ after transformation of SH groups in sulfonic acid groups. These thiol-functionalized hybrid materials were prepared mainly according to two methods. The first consists of grafting a mercaptopropyltrialkoxysilane onto the pore surface of ordered mesoporous silica.⁹ The second approach is a direct synthesis method, which involves the co-condensation of a mercaptopropyltrialkoxysilane with tetraethylorthosilicate (TEOS) in the presence of a structure-directing agent.^{1–5} However, both methods have their own limitations *i.e.* irregular repartition of thiol groups by grafting and low content of organic groups when the direct synthesis method is used. Recently, we have described a method allowing the self-organization thanks to van der Waals interactions of a bridged organosilica precursor with alkylene chains of different lengths [(MeO)₃Si(CH₂)_nSi(OMe)₃ with *n* = 12, 18 and 30], in aqueous solution during the sol–gel process.¹⁰ It was shown that the structure obtained is controlled by the alkylene chain length. The obtained materials are structured with lamellar phase for *n* = 12 and 18 while a hexagonal phase was obtained for *n* = 30.

Here we report an original method to synthesize lamellar structured materials highly thiol-functionalized. It involves an hydrolysis and polycondensation of bis silylated precursors with a disulfide core under weakly acidic conditions and without any surfactant followed by reduction of disulfide units to SH groups. Interestingly, the thiol centers of these materials are fully accessible as shown by adsorption of mercury(II) salts and their transformation to sulfonic acid.

Firstly, we prepared the mercaptoalkyltrimethoxysilanes (MeO)₃Si(CH₂)_nSH **1a–c** (**1a** *n* = 3, **1b** *n* = 5 and **1c** *n* = 11). **1a** was commercially available. Mercaptopentyltrimethoxysilane **1b**† and mercaptoundecyltrimethoxysilane **1c**‡ were synthesized as depicted in scheme 1: first long alkylene group carrying vinyl and



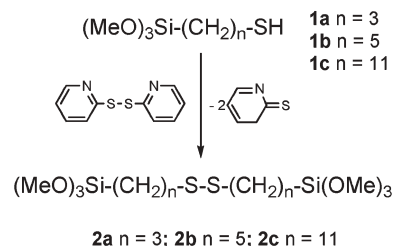
Scheme 1 Preparation of mercaptoalkyltrimethoxysilane **1b–c**.

bromo groups at the terminal positions were obtained in good yields by coupling the appropriate α, ω -dibromoalkane with one equivalent of Grignard reagent. Then, hydrosilylation of the vinyl groups gave rise to bromoalkyltrimethoxysilanes. Finally, treatment of the bromoalkyltrimethoxysilanes with a methanolic solution of sodium hydrosulfide (NaSH) afforded **1b** and **1c** in satisfactory yield after distillation. **1b–c** were fully characterized† by ¹H, ¹³C and ²⁹Si NMR spectroscopies as well as by elemental analysis.

The bis silylated precursors with disulfide core **2a**,¹¹ **2b**‡ and **2c**‡ were prepared by coupling two equivalents of **1a–c** in the presence of an excess of 2,2'-dithiopyridine in dichloromethane at room temperature¹² (Scheme 2).

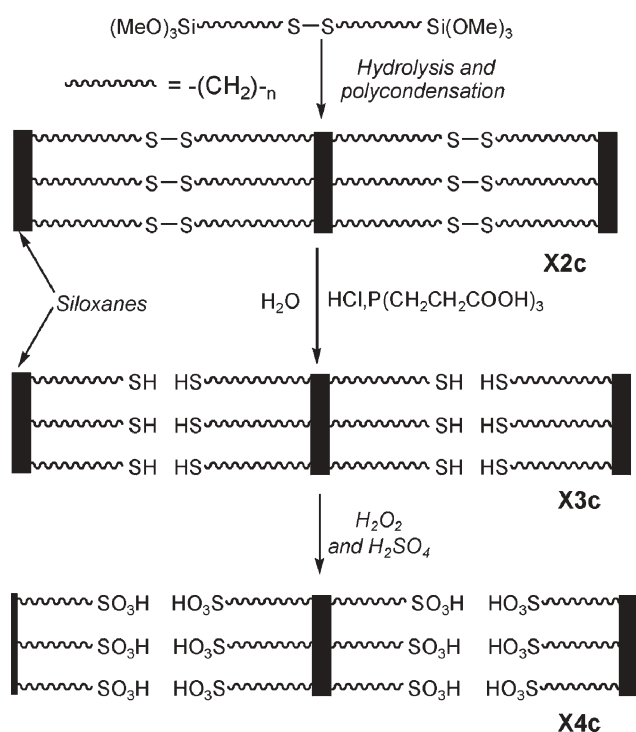
Materials were prepared by hydrolysis and polycondensation of bis-silylated precursors **2a–c** in aqueous solution (Scheme 3).

In a typical synthesis, 1.0 g of α, ω -bis-silylated precursor (CH₃)₃Si–(CH₂)_n–S–S–(CH₂)_n–Si(OCH₃)₃ was added to 30 mL of aqueous HCl solution (pH = 1.5) at 30 °C. The resulting mixture was stirred at 30 °C for 48 h. The corresponding solids **X2a**, **X2b** and **X2c** were recovered by filtration and washed successively with acetone (20 mL), ethanol (20 mL) and ether



Scheme 2 Preparation of disulfide precursors **2a–c**.

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† Electronic supplementary information (ESI) available: 1: ²⁹Si MAS NMR spectra of **X2c**; 2: XRD patterns of **X2a** and **X2b**; 3: XRD pattern of **X4c**. See DOI: 10.1039/b512537e



Scheme 3 Self-organisation of bridged organosilica with disulfide units and subsequent chemical transformation.

(10 mL). After drying (120 °C under vacuum for 12 h), they were collected as a white powder in high yields.

The CP-MAS ^{13}C NMR spectra of **X2a**, **X2b** (Fig. 1) and **X2c** revealed the incorporation of the organosiloxanes units. Resonances observed at 42.2 ppm and 13.8 ppm in all samples, were attributed to the CH_2S and CH_2Si , respectively. From elemental analysis, the S/Si ratio was found to be respectively, 0.98, 1.00 and 1.01 while the theoretical value was 1.00.

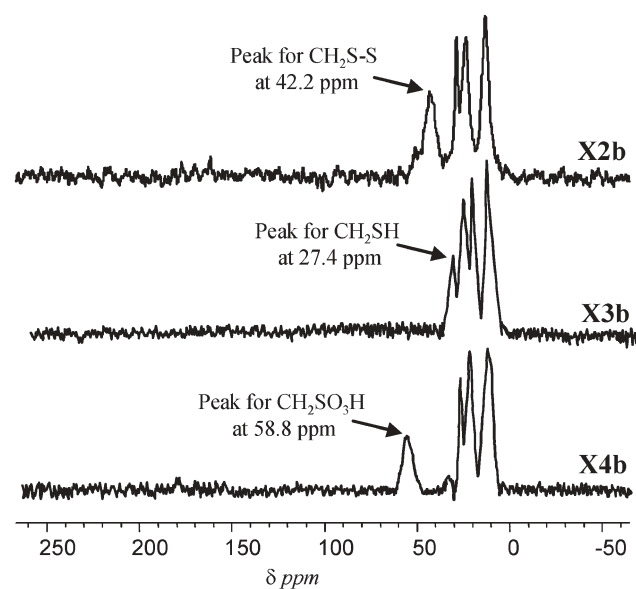


Fig. 1 CP-MAS ^{13}C NMR spectra of **X2b**, **X3b** and **X4b**, with peaks attributed to carbon situated in the α position from the sulfur atom showing clearly the chemical transformation.

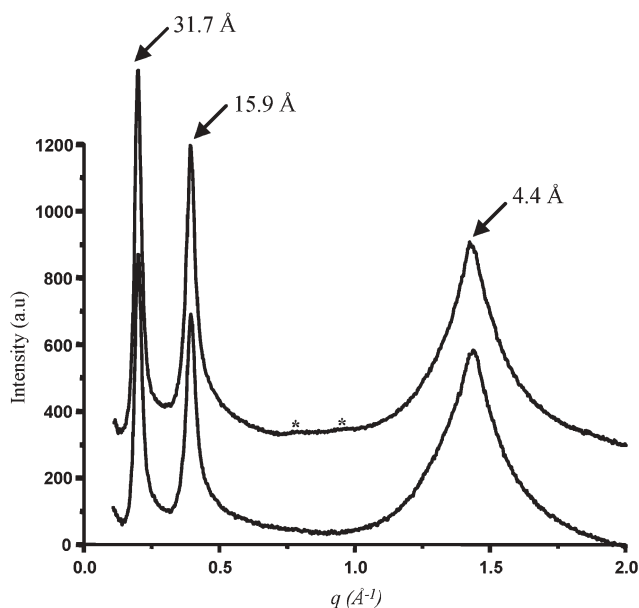


Fig. 2 XRD patterns of **X2c** (top) and **X3c** (bottom). Patterns are offset for clarity. * denote fourth- and fifth-order.

The ^{29}Si MAS NMR spectra indicated in all cases, that the materials **X2a–c** are well condensed (see ESI†, 1). The degree of polycondensation was 65% for **X2a**, 69% for **X2b** and 75% for **X2c** with T^2 $[\text{C}-\text{Si}(\text{OR})(\text{OSi})_2]$ signal at -58.5 ppm and T^3 $[\text{C}-\text{Si}(\text{OSi})_3]$ signal at -66.0 ppm as major peak. The absence of resonance corresponding to Q substructures (region near -100 ppm) denotes that there is no cleavage of Si–C bond during the sol–gel process.

The nitrogen adsorption measurements indicate that all the solids are nonporous ($S_{\text{BET}} < 10 \text{ m}^2 \text{ g}^{-1}$).

The X-ray powder diffraction (XRD) pattern of **X2c** (Fig. 2) exhibits well defined (100), (200) peaks at $q = 0.20$ and 0.42 \AA^{-1} , respectively. These peaks are characteristic of lamellar structure with 3.17 nm as the interlayer distance. The weak peaks observed at higher angles corresponding to 0.80, and 0.64 nm are attributed to fourth- and fifth-order diffractions indicating a material with well-ordered layered structure. The broad peak at 0.44 nm can be attributed to the distance between the flexible alkylene chains packing within the layers.^{10,13} The X-ray powder diffraction patterns of **X2a–b** (see ESI†, 2) show the same order with a lower resolution.

In order to reduce the disulfide (S–S) groups to mercapto (SH) groups, the materials **X2a–c** were treated with an aqueous solution of hydrogenotris(2-carboxyethyl)phosphonium chloride.¹⁴ The reactions were monitored by ^{31}P NMR spectroscopy. After 5 days at 55 °C, **X3a–c** were obtained with high yields (Scheme 3). Their solid state ^{13}C CP-MAS NMR spectra showed clearly the disappearance of the resonance at 42.2 ppm, characteristic of the carbon situated, in the α position from the disulfide bond. Simultaneously, a new resonance at 27.4 ppm appeared, which was assigned to carbon situated in the α position from the SH group^{6c} (Fig. 1).

Interestingly, the X-ray powder diffraction pattern of **X3c** showed that the lamellar structure of the material was maintained after chemical modification. The XRD pattern of **X3c** (Fig. 2) exhibits two intense peaks at 3.16 and 1.58 nm, values very similar

to those observed for **X2c** and attributed, respectively, to the first- and second-order. It is worth noting that the higher order disappears while the peak at 0.44 nm attributed to the interchain distance was maintained.

The accessibility of the SH functional groups in **X3a–b** was investigated by testing their chelating ability towards mercury(II) ions from aqueous solutions. The solids **X3a–b** were treated with an aqueous solution of HgCl₂ at room temperature arbitrarily for 12 h. The resulting solids were copiously washed with water to eliminate the non complexed salts and called **HgX3a–b**. The ratio of metal ions *per* thiol moieties in **HgX3a** and **HgX3b** was found to be around 1/3.5 and 1/2.6, respectively, from elemental analyses results. Thus, all materials had high mercury adsorption capacity (respectively, 2.2 and 2.5 mmol of Hg²⁺ *per* gram of **X3a** and **X3b**). These values are high in comparison with most of those obtained for thiol-modified mesoporous silica described in the literature^{6f} and similar to those of FMMS materials (2.5 mmol Hg²⁺ g⁻¹) described by Liu *et al.*^{6a,6b}

Finally, the mercapto groups were converted into sulfonic acid (SO₃H) groups by treatment of **X3a–c** with H₂O₂ solution followed by acidification with diluted H₂SO₄ solution to obtain **X4a–c** (Scheme 3). Their solid state ¹³C CP-MAS NMR spectra showed the diminution of the resonance at 27.4 ppm, characteristic of the carbon situated, in the α position from the SH group. Simultaneously, a new resonance at 58.8 ppm appeared, which was assigned to carbon situated in the α position from the SO₃H group (Fig. 1). XPS measurements and conductimetric titration of materials revealed that 75% of SH groups were transformed into SO₃H groups. The X-ray powder diffraction patterns of **X4a–c** showed a broad reflexion with low resolution (see ESI†, 3). That was probably due to the reduction of the contrast between the inorganic part and the organic chains due to replacement of SH groups by SO₃H groups.

In summary, we have described a new method for the formation of ordered and highly thiol-functionalized silica starting from bis silylated precursors containing disulfide units in alkylene chains. The high adsorption affinity of the SH groups towards mercury ions, renders these materials promising for removal of other heavy metal ions from aqueous solutions *i.e.* environmental remediation. Finally, the SO₃H groups could be useful for heterogeneous catalysts. This study describes a method leading to ordered hybrid materials by self-assembly thanks to van der Waals interactions.¹⁰ It is an innovative route for the structuration and functionalization, which leads to materials, different from those obtained through surfactant-directed assembly.

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Notes and references

† **1c**: To a solution of NaSH (24.40 mmol, 1.36 g) in anhydrous methanol (35 mL) was added a solution of 11-bromopentyltrimethoxysilane (16.20 mmol, 5.75 g) in anhydrous methanol (30 mL), under argon. The resulting solution was stirred for 14 h at room temperature. Methanol was removed under vacuum and the resulting residue was stirred in pentane (50 mL). After filtration of NaBr and NaSH, the filtrate was evaporated under vacuum. The crude product was purified by distillation (113 °C at

4.10⁻² mbar) to give a yellow liquid (4.29 g, 13.9 mmol, 86% yield). ¹H NMR (200 MHz, CDCl₃): 0.62 (2H, t, ²J_{H,H} = 8 Hz), 1.48 (16H, m), 1.70 (2H, tt, ²J_{H,H} = 6 and 7 Hz), 2.63 (2H, dd, ²J_{H,H} = 7 Hz), 3.58 (9H, s). ¹³C NMR (50 MHz, CDCl₃): 9.20 (CH₂-Si), 24.80 (CH₂-SH), 25.01 (CH₂-CH₂-Si), 30.21 to 30.65 (-CH₂-CH₂-CH₂-), 34.24 (CH₂-CH₂-SH), 51.60 (O-CH₃). ²⁹Si NMR (40 MHz, CDCl₃): -42.30. Anal. calcd. for C₁₄H₃₂O₃SSi: C 54.55, H 10.38, O 15.58, S 10.38, Si 9.10. Found: C 54.38, H 10.24, S 10.42, Si 9.08 (%). **1b**: ¹H NMR (200 MHz, CDCl₃): 0.67 (2H, t, ²J_{H,H} = 7 Hz), 1.44 (4H, m), 1.74 (2H, tt, ²J_{H,H} = 7 and 8 Hz), 2.50 (2H, dd, ²J_{H,H} = 8 Hz), 3.56 (9H, s). ¹³C NMR (50 MHz, CDCl₃): 9.38 (CH₂-Si), 23.98 (CH₂-SH), 24.89 (CH₂-CH₂-Si), 30.62 (CH₂-CH₂-SH), 34.06 (-CH₂-CH₂-CH₂-), 50.90 (O-CH₃). ²⁹Si NMR (40 MHz, CDCl₃): -43.10. Anal. calcd. for C₈H₂₀O₃SSi: C 42.86, H 9.93, O 21.43, S 14.29, Si 12.25. Found: C 43.01, H 9.88, S 14.28, Si 12.24 (%). **2c**: To a solution of 2,2'-dithiopyridine (4.87 mmol, 1.07 g) in anhydrous dichloromethane (15 mL) was added **1c** (9.74 mmol, 3.00 g), under argon. The resulting solution was stirred for 4 days at room temperature. Dichloromethane was removed under vacuum and petroleum ether (20 mL) was added. After filtration, the filtrate was evaporated and the obtained crude was distilled (153 °C at 3.10⁻² mbar) to give a yellow liquid (2.81 g, 4.58 mmol, 94% yield). ¹H NMR (200 MHz, CDCl₃): 0.69 (4H, t, ²J_{H,H} = 8 Hz), 1.37 (32H, m), 1.74 (4H, tt, ²J_{H,H} = 12 and 10 Hz), 2.72 (4H, dd, ²J_{H,H} = 12 Hz), 3.64 (18H, s). ¹³C NMR (50 MHz, CDCl₃): 9.55 (CH₂-Si), 23.00 (CH₂-CH₂-Si), 28.95 to 30.10 (-CH₂-CH₂-CH₂-), 33.57 (CH₂-CH₂-CH₂-Si), 39.62 (CH₂-S-S), 50.89 (O-CH₃). ²⁹Si NMR (40 MHz, CDCl₃): -42.30. Anal. calcd. for C₂₈H₆₂O₆S₂Si₂: C 54.72, H 10.10, O 15.64, S 10.42, Si 9.12. Found: C 54.78, H 10.08, S 10.53, Si 9.16 (%). **2b**: ¹H NMR (200 MHz, CDCl₃): 0.66 (4H, t, ²J_{H,H} = 10 Hz), 1.43 (8H, m), 1.69 (4H, tt, ²J_{H,H} = 13 et 11 Hz), 2.68 (4H, dd, ²J_{H,H} = 11 Hz), 3.60 (18H, s). ¹³C NMR (50 MHz, CDCl₃): 9.46 (CH₂-Si), 23.03 (CH₂-CH₂-Si), 29.24 (CH₂-CH₂-S-), 32.68 (CH₂-CH₂-CH₂-Si), 39.36 (CH₂-S-S), 50.88 (O-CH₃). ²⁹Si NMR (40 MHz, CDCl₃): -41.80. Anal. calcd. for C₁₆H₃₈O₃S₂Si₂: C 43.05, H 8.52, O 21.52, S 14.35, Si 12.56. Found: C 42.98, H 8.51, S 14.42, Si 12.51(%).

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