Electronic Supplementary Information

SH-Functionalized Cubic Mesostructured Silica as Support for Small Gold Nanoparticles

Arnaud Boullanger, Sébastien Clément, Violaine Mendez, Stéphane Daniele, Chloé Thieuleux, Ahmad Mehdi

Contents **Page**

---

1. **Characterization methods**

Elemental analyses were carried out by the "Service Central de Micro-Analyse du CNRS, Vernaison, France".

The nitrogen adsorption isotherms were measured at liquid temperature (77 K) using a Micromeritics Tristar 3000 analyser. Before the measurements, the samples were out gassed under vacuum for 12 h at 100 1C. The specific surface areas were calculated by the Brunauer-Emmett-Teller (BET) method (using 74 points and starting from 0.01 as value for the relative pressure) and the pore size distributions were determined by the DBdB method applied to the adsorption branch. It is worth noting that this method is considered to slightly undervalue the pore size for the pores inferior to 6 nm.[1]

Transmission Electron Microscopy (TEM) observations were carried out at 100 kV (JEOL 1200 EXII). Samples for TEM measurements were prepared by embedding the hybrid material in AGAR 100 resin, followed by ultramicrotomy techniques and deposition on copper grids.

Solid state NMR spectra for ^{29}Si and ^{13}C were recorded on a Varian VNMRS 300 Solid spectrometer at a magnetic field strength of 7.05 T. A 7.5 mm MAS probe was used with a spinning rate of 5 kHz. Single pulse experiments with a continuous wave ^{1}H decoupling were used for ^{29}Si NMR, with 2 μs π/2 pulse duration and a recycle delay of 60 s. A recycle delay of 200 s was found necessary to allow full ^{29}Si relaxation although this did not lead to any change in the relative ratio of the individual components on spectral decomposition. Thus, data with recycle delay of 60 s can be considered as quantitative. For ^{13}C NMR, CP MAS experiments with a continuous wave ^{1}H decoupling were acquired with 5 s recycle, 5 μs π/2 (1H) pulse duration and 3 ms contact time. The ^{29}Si and ^{13}C nuclei were referenced to TetraMethylSilane (TMS) at 0 ppm. Solid state NMR spectra were fitted using the Dmfit program.[2]

Diffuse reflectance UV-Visible (DRUV) spectra of the hybrid materials **M-SH^{5}** and **M-SH^{5Au}** were measured in the 350 – 800 nm range using $BaSO_4$ as reference with an integrating

---

[1] H. M. Kao, P. C. Chang, J. D. Wu, A. S. T. Chiang and C. H. Lee, *Microporous Mesoporous Mater.* 2006, **97**, 9

[2] D. Massiot, F. Fayon, M. Capron, I. King, S. Le Calve, B. Alonso, J. O. Durand, B. Bujoli, Z. H. Gan and G. Hoatson, *Magn. Reson. Chem.* 2002, **40**, 70.

sphere (Labsphere, North Sutton, USA). All UV-visible spectra were recorded on a Perkin Elmer Lambda 14 spectrophotometer.

2. Experimental Section

a. Materials

Tetraethoxysilane (TEOS), pluronic F-127 block copolymer, mercaptopropyltrimethoxysilane (MPTMS), monohydrated sodium acetylacetonate, sodium tetraborohydride were obtained from Aldrich and used as received without further purification. Chlorotetrahydrothiophene gold (I) was prepared according to a literature method.[3]

b. Preparation of the **M-SH^5**

2.00 g (0.16 mmol) of Pluronic F127, 7.19 g (123 mmol) of NaCl, 60 mL of permuted water and 20 mL of a 2M HCl solution were placed in a teflon bottle, which was then closed hermetically. After stirring vigorously for about 1.5 h, a clear solution was obtained. The bottle was then placed in a thermostated oil-bath at 40 °C. After stirring for 1 h, 7.96 g (38.3 mmol) of TEOS were first added to this mixture rather rapidly with a syringe followed immediately of 0.40 g (2.0 mmol) of MPTMS. The molar composition of the resulting mixture was the following MPTMS / TEOS / F127 / NaCl / H_2O / HCl was 1 / 19 / 0.08 / 60 / 1640 / 20. The mixture was further stirred vigorously at 40 °C for 20 h. After this time, a white “cloud” was observed. The closed bottle was then placed in an oven for 2 h at 110 °C. After decantation, the white precipitate was filtered off, washed 3 times with 30 mL of ethanol, then acetone. The powder was crushed in a mortar and dried under vacuum at 100 °C for 5 h. Surfactant was completely removed by extracting about 4 g of the as-synthesized material with a mixture of 30 mL of pyridine, 30 mL of permuted H_2O and 5 mL of a 2M HCl solution at 70 °C overnight. The pH has to be adjusted at 6-7 by addition of 2M HCl to avoid basic conditions, which could damage the silica. After washing three times with ethanol then acetone, followed by a pulverizing step, the solid was dried at 100 °C under vacuum for 6 hours giving rise to **M-SH^5** as white powder in about 85 % yield.

c. Preparation of the **M-SH^{5Au}**

In a typical synthesis, 50 mg (0.155 mmol) of chlorotetrahydrothiophene gold (I) and 10 mL of THF were placed in a 25 mL-round-bottom flask under argon. The mixture was stirred till

---

[3] R. Uson, A. Laguna, M. Laguna, D. A.; Briggs, H. H. Murray and J. P. Fackler, *Inorg. Synth.* 2007, **26**, 85.

dissolution. In parallel, 1.0 g (0.79 mmol) of **M-SH^{5}**, 25 mg (0.179 mmol) of monohydrated sodium acetylacetonate and 50 mL of THF were introduced in a Schlenk under argon. The gold solution was then transferred with a syringe into the Schlenk tube and the mixture was stirred at room temperature for 2 h to impregnate the solid of the gold precursor. The impregnated material was filtered-off and washed three times by 20 mL of THF under argon. The collected white powder was dried under vacuum for 30 minutes before to be placed in another Schlenk with argon and 50 mL of ethanol. The gold precursor impregnated inside the solid was reduced with 10 mL of ethanol containing 125 mg (3.31 mmol) of sodium tetraborohydride. The mixture turned immediately to brown and was let under stirring overnight. The solid **M-SH^{5Au}** was finally filtered-off, washed three times by 20 mL of ethanol and dried under vacuum at 50 °C for 5 h. Anal. calcd.: Au. 2.9 % Found 2.7 %; Si/S 20.0. Found 19.0.; S/Au 5.0. Found 4.7.

d. Catalytic evaluation of **M-SH^{5Au}**

Catalytic evaluation is carried out in round-bottom flasks under conditions previously optimized for the aerobic epoxidation of trans-stilbene. Trans-stilbene (substrate, 1 mmol), the gold catalyst (14.8 mg, Au: 2 µmol), methylcyclohexane (solvent, 20 mL/155 mmol) and tert-butyl hydroperoxide (initiator, 0.05 mmol/7 µL of a 70% TBHP in water Alfa Aesar solution) are stirred together at 80 °C for 60 h. The reaction is carried out in air at atmospheric pressure; the mixture is simply exposed to ambient air throughout the reaction. Products are analyzed by gas chromatography (Shimadzu GC-2014), using an Equity TMS 30 m × 0.25 mm × 0.25 µm column programmed from 60 °C to 180 °C, an injector and FID detector set at 280 °C and 200 °C respectively, and He as carrier gas (26.6 mL min^{-1}) and high performance liquid chromatography (Perkin-Elmer HPLC Series 200), using a Spheri-5 RP-18 220 mm × 4.6 mm × 3 µm C18 reverse-phase column, an acetonitrile/water mobile phase mixture at a constant flow rate of 1.0 mL min^{-1} and a Series 200 UV detector set at 250 nm. External calibration is carried out by injecting a standard solution containing trans-stilbene (96%, Sigma–Aldrich) and trans-stilbene oxide (99%, Aldrich) in acetonitrile.

Trans-stilbene conversion and trans-stilbene oxide yield are ratios of the number of mole of stilbene converted and the number of mole of epoxide formed both over the initial number of mole of stilbene introduced at the beginning of the reaction. Selectivity is defined as the ratio of yield over conversion.

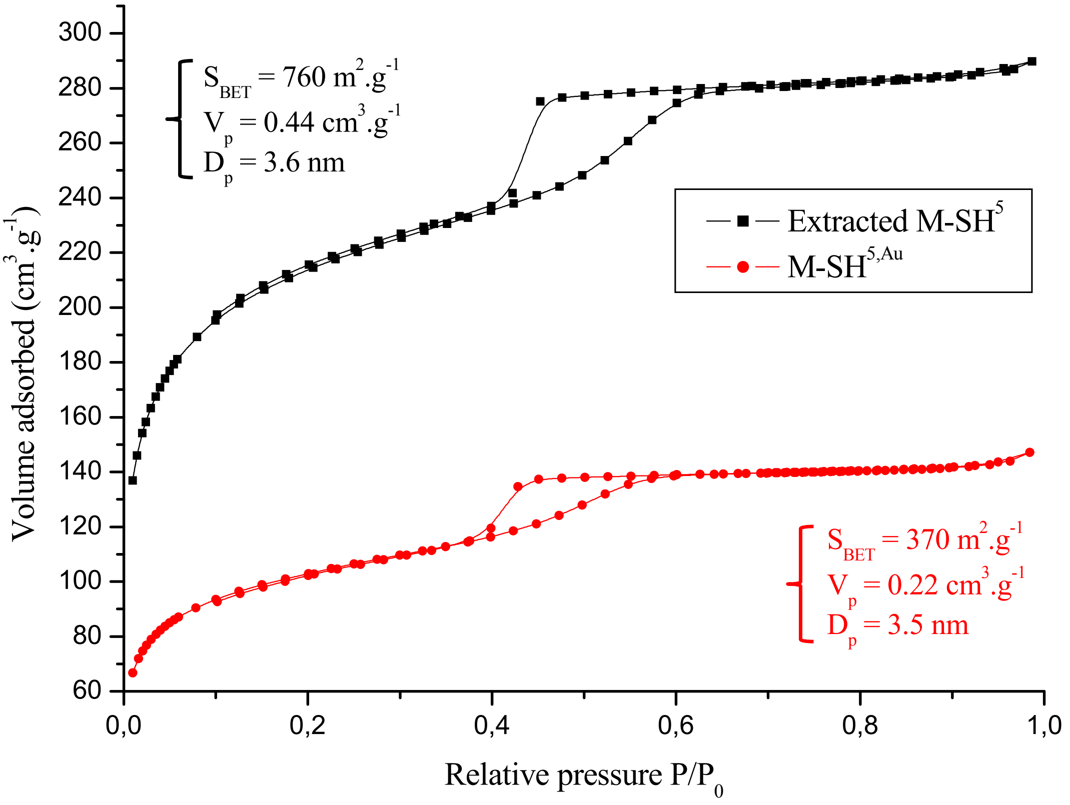

Fig. S1. Nitrogen adsorption-desorption isotherms at 77 K for extracted **M-SH^5** (*top*) and **M-SH^{5Au}** (*down*).

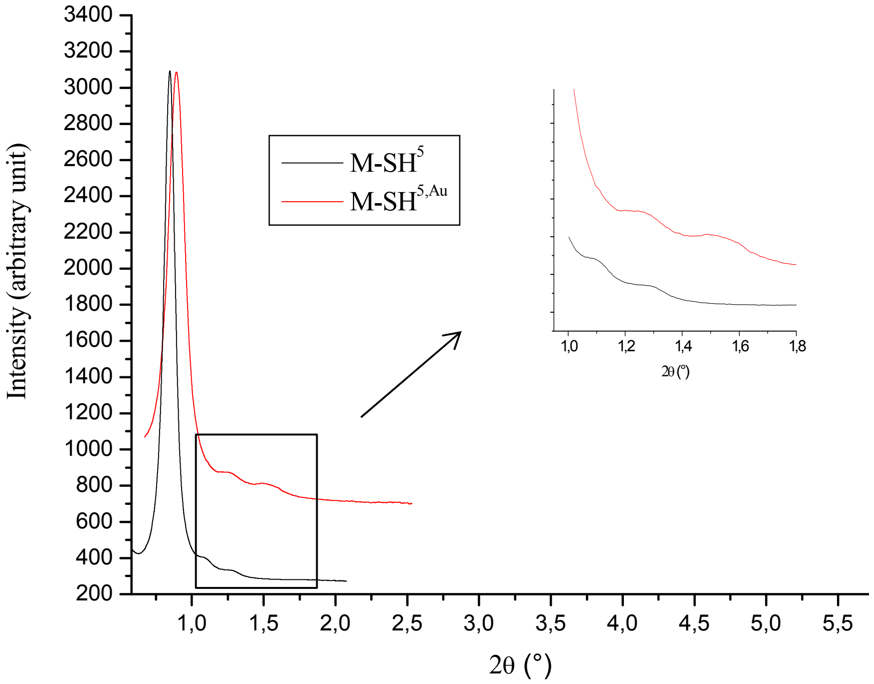

Fig. S2. Powder XRD patterns for extracted **M-SH^5** (*dark*) and for material **M-SH^{5Au}** containing AuNPs (*red*).

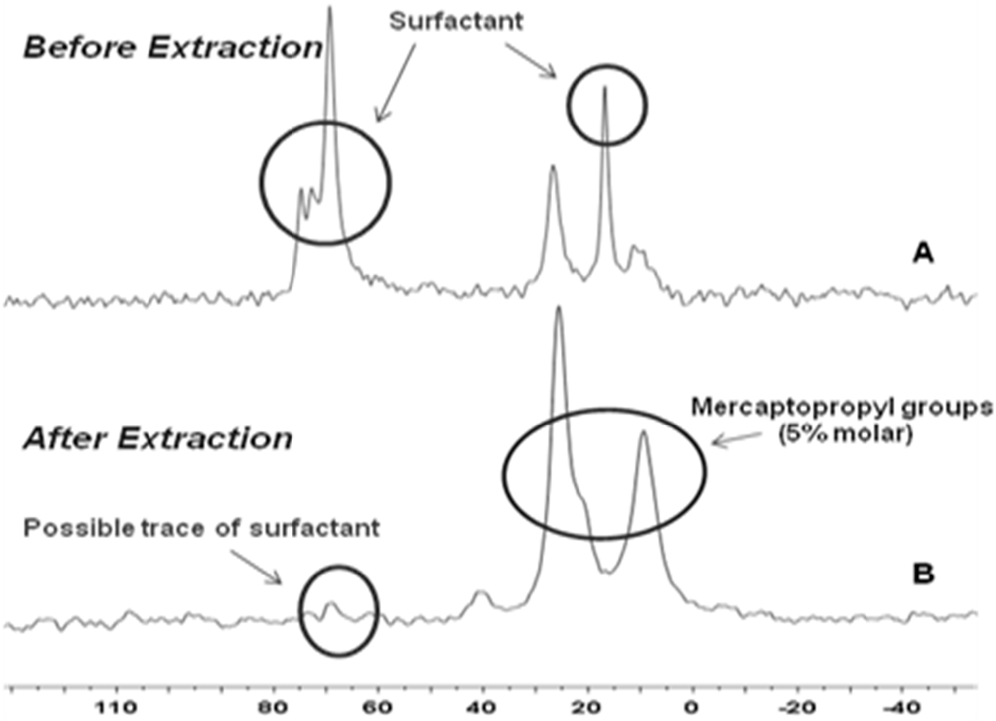

Fig. S3. ^{13}C CP-MAS NMR spectra of **M-SH^5**. (A) as-made material, (B) extracted material.

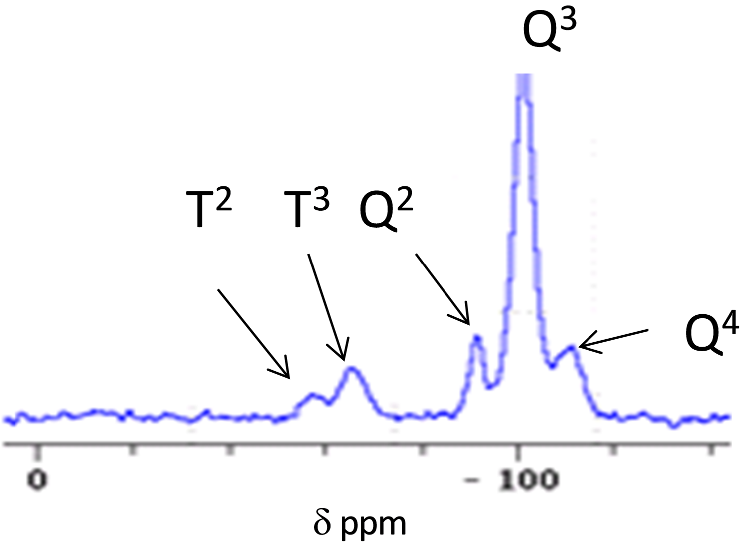

Figure S4. ^{29}Si CP-MAS NMR spectrum of **M-SH^5**.

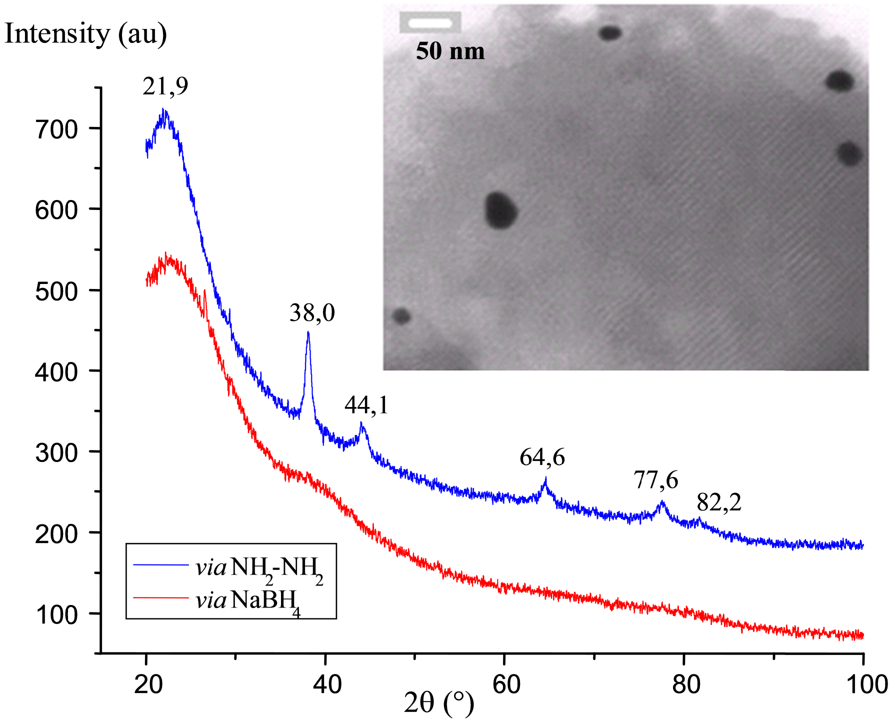

Fig. S5. X-Ray Diffraction patterns of **M-SH**^{5Au} by using NaBH4 (*red*) or hydrazine (*blue*). The inset shows the TEM image of **M-SH**^{5Au} after hydrotreatment (presence of large AuNPs).

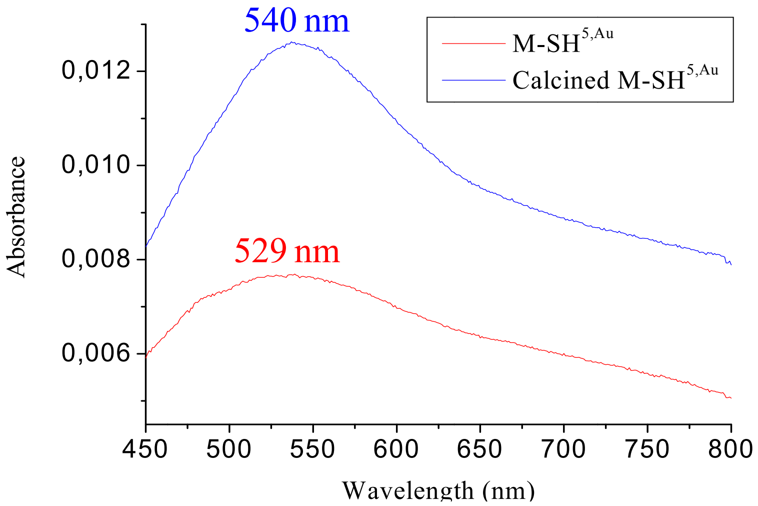

Fig. S6. UV-visible spectra for **M-SH**^{5Au} before and after calcination.