

**A New Nanometric Hybrid System Based on Gold Nanoparticles and
Heteropolyanions**

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Experimental Section

Samples preparation : -The organosilyl derivative [γ -SiW₁₀O₃₆(RSi)₂O]⁴⁻ [R = -C₃H₆SH] ([POM(SH₂)]⁴⁻) is prepared as described in detail elsewhere^[1] : 0.28 mL (1.33.10⁻³ mmol) of HSC₃H₆-Si(OMe)₃ is added to a solution of 2 g (6.66.10⁻⁴ mmol) of K₈[γ -SiW₁₀O₃₆].12H₂O^[2] and 0.64 g of Bu₄NBr in 40 mL of CH₃CN and 10 mL of H₂O at 0°C. Then, the mixture is acidified with 1.2 mL of a 12 M solution of chlorhydric acid and the solution is stirred overnight. The crude compound is obtained after evaporation of the organic solution. Yield: 3.0 g (90.9 %). C₅₄H₁₂₃N₃Si₃S₂W₁₀O₃₇ (%): calcd C 19.11, H 3.65, N 1.24, S 1.89, Si 2.48, O 17.44, W 54.18; found C 19.95, H 3.78, N 1.30, S 1.86, Si 2.44, O 17.21, W 53.45; - IR (KBr) : \tilde{n} = 2563 cm⁻¹ [vs, v(SH)], 1384 [m, δ (CH)], 1162 [s, v(SiC)], 1100 [s, v(SiO)], 1051 [w, v(SiO)], 962-738 [vs, v(WO)], 544 [vw, δ (SiO)], 408 [vw, δ (WO)], 366 [vw, δ (WO)]. ¹⁸³W NMR (ppm); δ = -107.6 (2), -136.8 (1), -141.8 (2).

- 4-5 nm Gold nanoparticles : 0.9 ml of HAuCl₄ (0.1 mol.l⁻¹) in 2.1 ml of water are added to 8 ml of Noct₄Br (0.05 mol.l⁻¹) in toluen. After, separation of the red/orange organic phase, 2.5 ml of an aqueous solution of NaBH₄ (0.4 mol.l⁻¹) are added dropwise. The resulting mixture turns rapidly to a purple color and is stirred during four hours. UV/Vis: λ_{max} = 520 nm.

- 8 nm Gold nanoparticles : The experimental procedure is similar to the previous synthesis but the concentration of Noct_4Br in toluen is fixed to 0.1 mol.l^{-1} . UV/Vis: $\lambda_{\max} = 528 \text{ nm}$.

? 12 nm Gold nanoparticles : An aqueous solution (20 ml H_2O deionized) of trisodium citrate ($4.10^{-3} \text{ mol.l}^{-1}$) and of reducing agent (NaBH_4 , $5.72.10^{-4} \text{ mol.l}^{-1}$) is added to an aqueous solution of HAuCl_4 ($4.10^{-3} \text{ mol.l}^{-1}$, 20 ml H_2O deionized). The resulting mixture is stirred during four hours. UV/Vis: $\lambda_{\max} = 530 \text{ nm}$.

- Gold particles functionnalized by $[\text{POM}(\text{SH}_2)^{4-}]$:

- From organic medium : This solution of particles in toluen is added dropwise into an acetonitril solution of $[\text{POM}(\text{SH}_2)^{4-}]$ (48.10^{-3} g , 20 ml). The resulting solution is stirred overnight. After total evaporation of the organic solution, the crude product is solubized in a small volume of acetonitril and precipitated by ethanol. Then the product is precipitated two times by water. The dark/purple product can be totally dispersed in different organic solvents such as DMF, DMSO or CH_3CN . UV/Vis of $\text{POM}(\text{SH}_2)$ -Au-nanoparticles of 4-5 nm : $\lambda_{\max} = 520 \text{ nm}$ and of 8 nm : $\lambda_{\max} = 528.5 \text{ nm}$
- From aqueous medium : 40 ml of the solution of gold nanoparticles with citrate is added dropwise in 100 ml of acetonitril containing $42.6.10^{-3} \text{ g}$ of $[\text{POM}(\text{SH}_2)^{4-}]$. The mixture is stirred overnight. Gold functionnalized nanoparticles are precipitated by evaporation of the organic solvent. The precipitated nanocrystals are filtered, re-dissolved in a minimum of acetonitril and re-precipitated by addition of H_2O (40 ml). The precipitate is washed with EtOH and ether and dried in air. ^{183}W NMR (ppm) : $\text{d} = -107.2$ (2), -136.4 (1), -140.9 (2). UV/Vis : $\lambda_{\max} = 530 \text{ nm}$.

IR (KBr) spectra of $\text{POM}(\text{SH}_2)$ -Au-nanoparticles: $\tilde{\nu} = 1383$ [m, $?\text{(CH)}$], 1160 [s, $?\text{(SiC)}$], 1098 [s, $?\text{(SiO)}$], 1049 [vw, $?\text{(SiO)}$], 961-736 [vs, $?\text{(WO)}$], 544 [vw, $?\text{(SiO)}$], 409 [vw, $?\text{(WO)}$], 366 [vw, $?\text{(WO)}$].

Physical measurements

The compound $\text{g-K}_8[\text{SiW}_{10}\text{O}_{36}].8\text{H}_2\text{O}$ is prepared according to the literature.^[1] Other reagents, $[\text{RSi}(\text{OMe})_3]$ and solvents are purchased from Aldrich and used as received. ? Elemental

analyses are performed by the " Service central de microanalyses du CNRS ", Vernaison, France. - The IR spectra (4000-250 cm^{-1}) are recorded on a Bio-Rad FTS 165 IR FT spectrometer with compounds and dried hydroferrogels sampled in KBr pellets. - Crystalline structure of particles and their average diameter are determined using X-ray diffraction. Powders X-Ray diffraction patterns are obtained with a Phillips PW1130 diffractometer using Co $\text{K}\alpha$ radiation ($\lambda = 1.7902 \text{ \AA}$). The average crystallite size of the particles is calculated using Scherrer formula on the main reflection peak - Visualization of functionnalized gold nanoparticles are performed with a transmission electron microscope (TEM) (microscope JEOL 100 CX2) in the " Centre Régional de Mesures Physiques " Paris 6: a drop of an acetonitril solution deposited and dried on a grid. - The 12.5 MHz ^{183}W NMR spectra are recorded at 300 K on DMF/CD₃CN (90/10, v/v) solutions in 10 mm o.d. tubes on Bruker AC300 spectrometer equipped with a low-frequency special VSP probehead. The chemical shifts are given with respect to 2M Na₂WO₄ aqueous solution and are determined by the substitution method using a saturated D₂O solution of tungstosilicic acid H₂SiW₁₂O₄₀ as secondary standard ($d = -103.8$). - UV/Vis spectra are recorded on CH₃CN-dissolved samples, using a Shimadzu UV-2101 PC scanning spectrophotometer, and the experimental data were corrected for CH₃CN backgrond absorption.

[1] C. R. Mayer, I. Fournier, R. Thouvenot, *Chem. Eur. Jour.* **2000**, 6, 105.

[2] J. Canny, A. Tézé, R. Thouvenot, G. Hervé, *Inorg. Chem.* **1986**, 25, 2114.

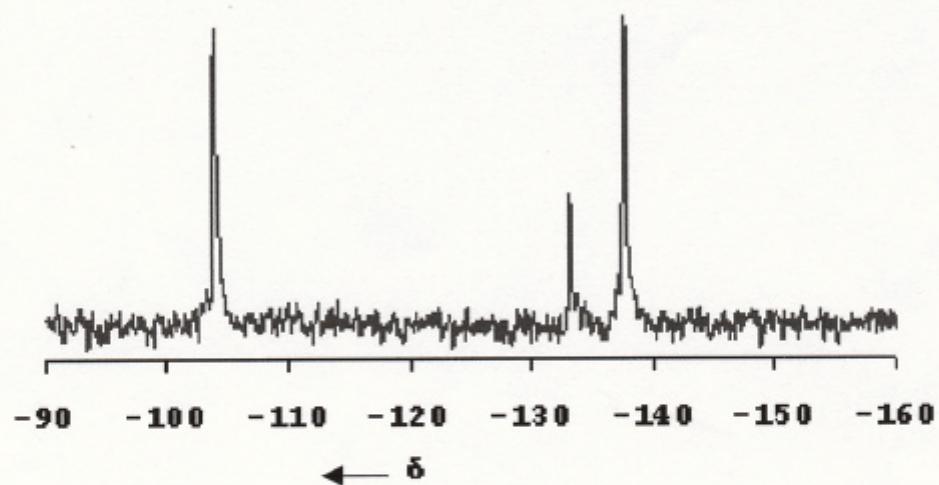


Figure S1

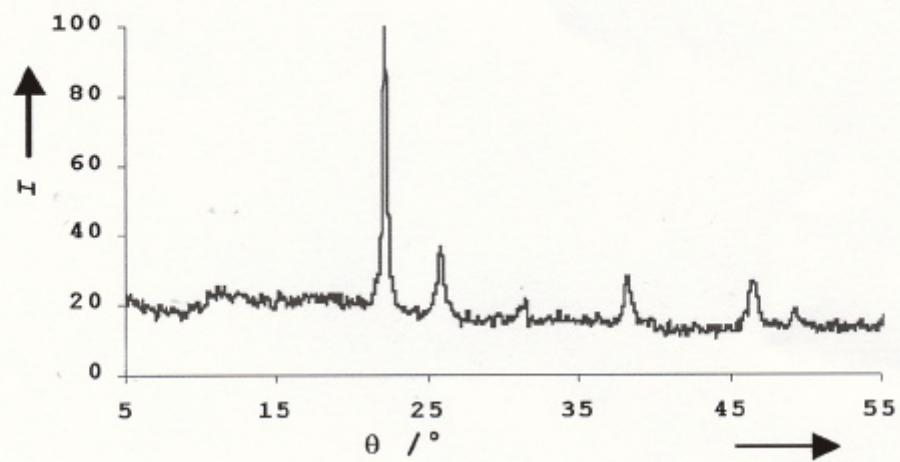


Figure S2

Legend for Figures:

Figure S1. ^{183}W NMR (12.5 MHz) spectra of hybrid POM(SH_2)-Au-nanoparticles of 12 nm obtained from citrate solution - decoupled full spectrum.

Figure S2. X-Ray diffraction powder pattern of hybrid POM(SH_2)-Au-nanoparticles of 12 nm.