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

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## Experimental Section

Samples preparation : -The organosilyl derivative [ $\gamma$ -SiW<sub>10</sub>O<sub>36</sub>(RSi)<sub>2</sub>O]<sup>4-</sup> [R = -C<sub>3</sub>H<sub>6</sub>SH] ([POM(SH<sub>2</sub>)]<sup>4-</sup>) is prepared as described in detail elsewhere <sup>[1]</sup> : 0.28 mL (1.33.10<sup>-3</sup> mmol) of HSC<sub>3</sub>H<sub>6</sub>-Si(OMe)<sub>3</sub> is added to a solution of 2 g (6.66.10<sup>-4</sup> mmol) of K<sub>8</sub>[ $\gamma$ -SiW<sub>10</sub>O<sub>36</sub>].12H<sub>2</sub>O <sup>[2]</sup> and 0.64 g of Bu<sub>4</sub>NBr in 40 mL of CH<sub>3</sub>CN and 10 mL of H<sub>2</sub>O 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 %). C<sub>54</sub>H<sub>123</sub>N<sub>3</sub>Si<sub>3</sub>S<sub>2</sub>W<sub>10</sub>O<sub>37</sub> (%): 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) :  $\tilde{\nu}$  = 2563 cm<sup>-1</sup> [vs, v(SH)], 1384 [m,  $\delta$ (CH)], 1162 [s, v(SiC)], 1100 [s, v(SiO)], 1051 [w, v(SiO)], 962-738 [vs, v(WO)], 544 [vw,  $\delta$ (SiO)], 408 [vw,  $\delta$ (WO)], 366 [vw,  $\delta$ (WO)]. <sup>183</sup>W NMR (ppm);  $\delta$  = -107.6 (2), -136.8 (1), -141.8 (2).

- 4-5 nm Gold nanoparticles : 0.9 ml of HAuCl<sub>4</sub> (0.1 mol.l<sup>-1</sup>) in 2.1 ml of water are added to 8 ml of Noct<sub>4</sub>Br (0.05 mol.l<sup>-1</sup>) in toluen. After, separation of the red/orange organic phase, 2.5 ml of an aqueous solution of NaBH<sub>4</sub> (0.4 mol.l<sup>-1</sup>) are added dropwise. The resulting mixture turns rapidly to a purple color and is stirred during four hours. UV/Vis:  $\lambda_{\text{max}}$  = 520 nm.

- 8 nm Gold nanoparticles : The experimental procedure is similar to the previous synthesis but the concentration of  $\text{NaAuCl}_4$  in toluene is fixed to  $0.1 \text{ mol.l}^{-1}$ . UV/Vis:  $\lambda_{\text{max}} = 528 \text{ nm}$ .

? 12 nm Gold nanoparticles : An aqueous solution (20 ml  $\text{H}_2\text{O}$  deionized) of trisodium citrate ( $4.10^{-3} \text{ mol.l}^{-1}$ ) and of reducing agent ( $\text{NaBH}_4$ ,  $5.72.10^{-4} \text{ mol.l}^{-1}$ ) is added to an aqueous solution of  $\text{HAuCl}_4$  ( $4.10^{-3} \text{ mol.l}^{-1}$ , 20 ml  $\text{H}_2\text{O}$  deionized). The resulting mixture is stirred during four hours. UV/Vis:  $\lambda_{\text{max}} = 530 \text{ nm}$ .

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

- From organic medium : This solution of particles in toluene is added dropwise into an acetonitrile solution of  $[\text{POM}(\text{SH}_2)^{4-}]$  ( $48.10^{-3} \text{ g}$ , 20 ml). The resulting solution is stirred overnight. After total evaporation of the organic solution, the crude product is solubilized in a small volume of acetonitrile 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  $\text{CH}_3\text{CN}$ . UV/Vis of  $\text{POM}(\text{SH}_2)$ -Au-nanoparticles of 4-5 nm :  $\lambda_{\text{max}} = 520 \text{ nm}$  and of 8 nm :  $\lambda_{\text{max}} = 528.5 \text{ nm}$
- From aqueous medium : 40 ml of the solution of gold nanoparticles with citrate is added dropwise in 100 ml of acetonitrile containing  $42.6.10^{-3} \text{ g}$  of  $[\text{POM}(\text{SH}_2)^{4-}]$ . The mixture is stirred overnight. Gold functionalized nanoparticles are precipitated by evaporation of the organic solvent. The precipitated nanocrystals are filtered, re-dissolved in a minimum of acetonitrile and re-precipitated by addition of  $\text{H}_2\text{O}$  (40 ml). The precipitate is washed with EtOH and ether and dried in air.  $^{183}\text{W}$  NMR (ppm);  $\delta = -107.2$  (2), -136.4 (1), -140.9 (2). UV/Vis :  $\lambda_{\text{max}} = 530 \text{ nm}$ .

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

### Physical measurements

The compound  $\mathbf{g}\text{-K}_8[\text{SiW}_{10}\text{O}_{36}].8\text{H}_2\text{O}$  is prepared according to the literature.<sup>[1]</sup> 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  $\text{cm}^{-1}$ ) 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  $K\alpha$  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 fonctionnalized 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  $^{183}\text{W}$  NMR spectra are recorded at 300 K on DMF/ $\text{CD}_3\text{CN}$  (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  $\text{Na}_2\text{WO}_4$  aqueous solution and are determined by the substitution method using a saturated  $\text{D}_2\text{O}$  solution of tungstosilicic acid  $\text{H}_2\text{SiW}_{12}\text{O}_{40}$  as secondary standard ( $\delta = -103.8$ ). - UV/Vis spectra are recorded on  $\text{CH}_3\text{CN}$ -dissolved samples, using a Shimadzu UV-2101 PC scanning spectrophotometer, and the experimental data were corrected for  $\text{CH}_3\text{CN}$  background 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.

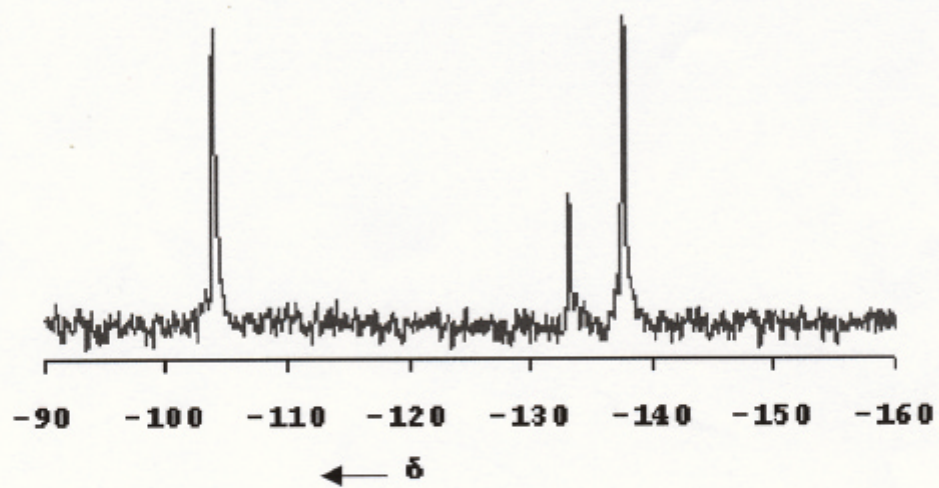


Figure S1

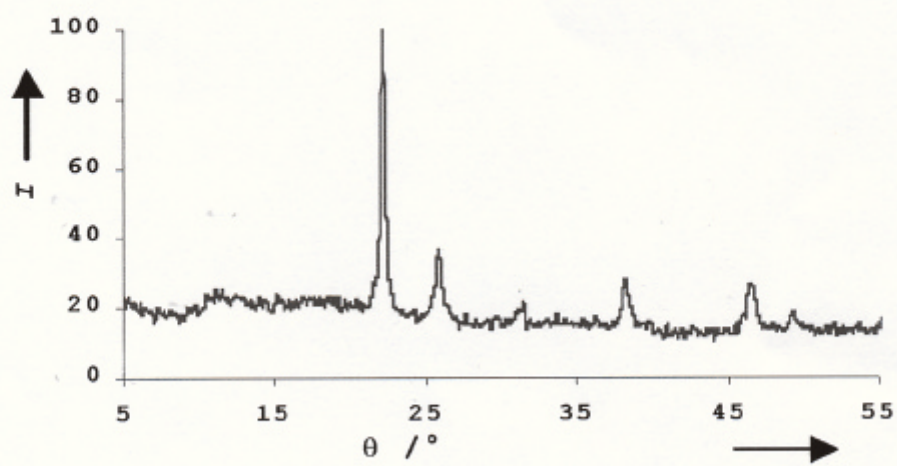


Figure S2

### **Legend for Figures:**

Figure S1.  $^{183}\text{W}$  NMR (12.5 MHz) spectra of hybrid POM(SH<sub>2</sub>)-Au-nanoparticles of 12 nm obtained from citrate solution - decoupled full spectrum.

Figure S2. X-Ray diffraction powder pattern of hybrid POM(SH<sub>2</sub>)-Au-nanoparticles of 12 nm.