

Supplementary Information

Solubility switch of gold nanoparticles through hydrogen bond association

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General methods:

^1H , ^{19}F and ^{13}C NMR spectra were obtained on a Brücker 200, 300 or 400 spectrometer. Chemical shifts δ are given in ppm relative to TMS, as internal standard for ^1H and ^{13}C NMR, and relative to CFCl_3 ^{19}F NMR. Coupling constant J are measured in Hz.

Elemental analyses of gold nanoparticles were performed at the Service Central d'Analyses of CNRS in Vernaison, France.

TEM micrographs of nanoparticles were taken on a TEM Philips EM208 (1996) equipped with a CCD video camera AMT at the Centre Commun de Microscopie Electronique (CCME) at the Université-Paris Sud, Orsay, France. The TEM micrographs were analysed with ImageJ software.

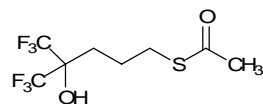
Materials:

All chemicals were used as provided without further purification. 1,1,1-trifluoro-2-(trifluoromethyl)pent-4-en-2-ol (AllylHFIP **1**) was provided by Central Glass Co. Ltd. Thioacetic acid and $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ were purchased from Acros, and each bottle was used entirely for a single experiment.

Monitoring of the reactions:

The conversion of the fluorinated substrates into products was measured by integration of the trifluoromethyl signals by ^{19}F NMR, directly from the reaction mixture.

Synthesis of the thioester **2**:



A round bottom flask was charged with thioacetic acid (5 g, 65.8 mmol) and **1** (2 g, 98.7 mmol) in dichloroethane (40 mL) and heated to reflux under argon atmosphere. After 15 minutes of reflux, AIBN (540 mg, 3.3 mmol) was added. The reaction was complete after 6 hours, and then the solvent was distilled from the reaction mixture to provide the product **2** as a stinky colorless liquid in a 98% yield (18.4 g).

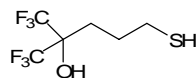
^1H NMR (CDCl_3 , 200 MHz), δ : 1.85 (m, 2H); 1.95 (m, 2H); 2.31 (s, 3H); 2.87 (t, $J=7.2$, 2H); 4.63 (s, 1H).

^{13}C NMR (CDCl_3 , 75 MHz), δ : 22.2; 28.9; 29.1; 30.3; 76.1 (hept, $J=29.1$); 123.2 (q, $J=290$); 198.1.

^{19}F NMR (CDCl_3 , 188 MHz), δ : -77.22 (s).

APCI m/z (rel. int.): 285 $[\text{M}+\text{H}]^+$ (100).

Synthesis of the thiol **3**:



The thioester **2** (2.84 g, 10 mmol) was dissolved in dry THF (30 mL) under argon atmosphere and cooled to 0 °C. Then LiAlH_4 (1.52 g, 40 mmol) was added portionwise at 0 °C over 20 min. and then warmed to room temperature. After completion of the reaction (1 h), the solution was cooled to -78 °C and then hydrolysed with water (30 mL). The mixture was extracted with AcOEt (3 x 50 mL), the combined organic phases were dried (MgSO_4), filtered and the solvents were finally evaporated to afford **3** as a stinky colorless liquid (2.4 g, 99% yield).

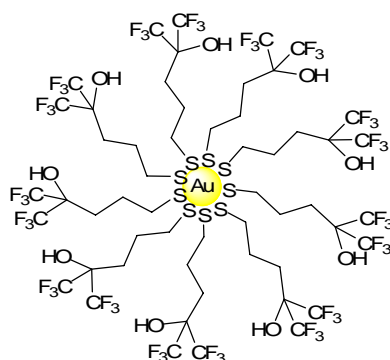
^1H NMR (CDCl_3 , 300 MHz), δ : 1.39 (t, $J=8.1$, SH); 1.86 (m, 2H); 2.03 (m, 2H); 2.55 (dt, $J=8.1$, 7.0, 2H); 4.38 (s, 1H).

^{13}C NMR (CDCl_3 , 75 MHz), δ : 24.5; 25.3; 26.1; 76.0 (hept, $J=29.1$); 123.2 (q, $J=291$).

^{19}F NMR (CDCl_3 , 188 MHz), δ : -77.15 (s).

APCI m/z (rel. int.): 483 $[2\text{M}-2+\text{H}]^+$ (100).

Synthesis of HFIP-gold nanoparticles (HFIP-AuNPs):



The thiol **3** (650 mg, 5 mmol) was dissolved in methanol (350 mL) with glacial acetic acid (7.5 mL) and $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (788 mg, 2 mmol). To this mixture was added a freshly prepared 0.4 M aqueous solution of NaBH_4 (75 mL; 30 mmol) under stirring. After one hour, the solvent was removed under vacuum and the residue was washed with water and CH_2Cl_2 to afford a sticky brown solid (450mg).

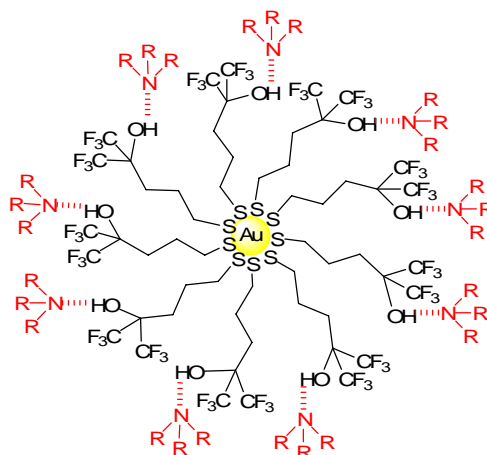
^1H NMR (CD_3OD , 300 MHz), δ : 2.00 (m, 4H); 2.76 (t, $J=6.7$, 2H).

^{19}F NMR (CD_3OD , 376 MHz), δ : -79.26 (s).

Elemental analysis (%): Au = 72.96; S = 3.79.

Nanoparticle size obtained by TEM: 2.8 ± 1.4 (\approx 410 Au atoms and 130 ligands *per* nanoparticle).

General procedure for complexes formation of HFIP-AuNPs with amines:



HFIP-AuNPs (20 mg) were dissolved in ethyl acetate and a solution of amine in ethyl acetate was added dropwise. The complex is formed as a dark-brown powder while the amine is added. AcOEt was evaporated and the excess of amine was eliminated by washing with water and a suitable organic solvent.

HFIP-AuNPs/piperazine complex:

^1H NMR (CD_3OD , 300 MHz), δ : 2.04 (m, 4H); 2.72 (s, 0.4 \times 8H); 3.05 (m, 2H).

^{19}F NMR (CD_3OD , 376 MHz), δ : -77.75 (s).

Elemental analysis (%): Au = 71.51; S = 4.07; N = 1.43.

Nanoparticle size obtained by TEM: 2.8 ± 1.9 (≈ 0.4 piperazines *per* alcohol).

HFIP-AuNPs/DABCO complex:

^1H NMR (CD_3OD , 300 MHz), δ : 2.12 (m, 4H); 2.88 (s, 0.3 \times 12H); 3.01 (m, 2H).

^{19}F NMR (CD_3OD , 376 MHz), δ : -77.50 (s).

Elemental analysis (%): Au = 72.18; S = 3.50; N = 1.01.

Nanoparticle size obtained by TEM: 2.8 ± 1.3 (≈ 0.35 DABCO *per* alcohol).

HFIP-AuNPs/tributylamine complex:

^1H NMR (CD_3OD , 300 MHz), δ : 1.07 (t, $J=7.3$, 0.3 \times 9H); 1.46 (pent, $J=7.4$, 0.3 \times 6H); 1.73 (m, 0.3 \times 6H); 2.03 (m, 4H and 0.3 \times 6H); 2.76 (t, $J=6.7$, 2H).

^{19}F NMR (CD_3OD , 376 MHz), δ : -79.13 (s).

Elemental analysis (%): Au = 49.13; S = 4.32; N = 0.56.

Nanoparticle size obtained by TEM: 2.9 ± 1.6 (≈ 0.3 amines *per* alcohol).

HFIP-AuNPs/tridodecylamine complex:

^1H NMR (CD_3OD , 300 MHz), δ : 0.93 (t, $J=6.7$, 0.3 \times 9H); 1.33 (m, 0.3 \times 60H); 2.08 (m, 4H and 0.3 \times 6H); 2.88 (m, 2H).

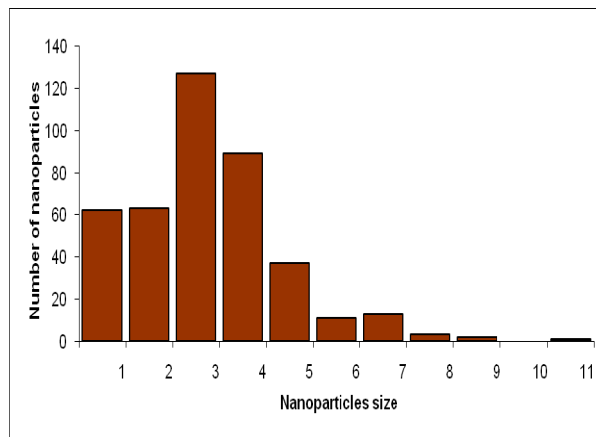
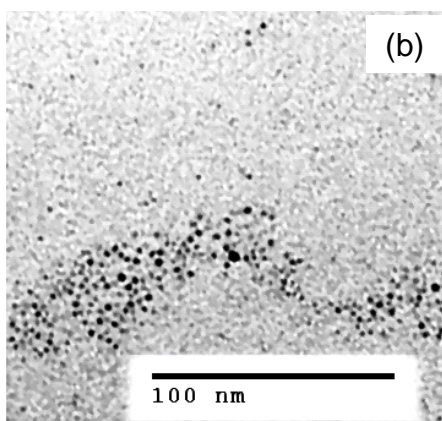
^{19}F NMR (CD_3OD , 376 MHz), δ : -79.23 (s).

Elemental analysis (%): Au = 47.19; S = 4.66; N = 0.52.

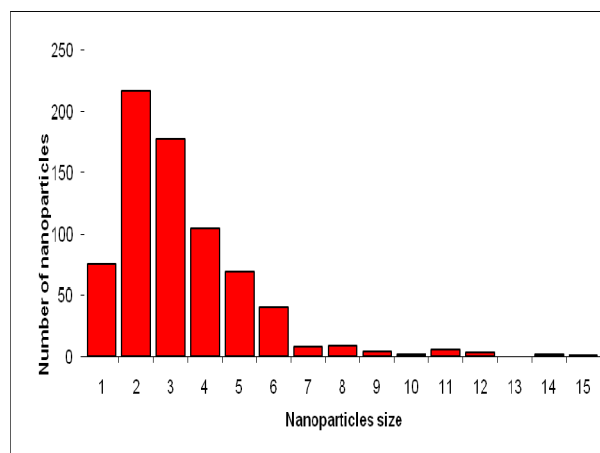
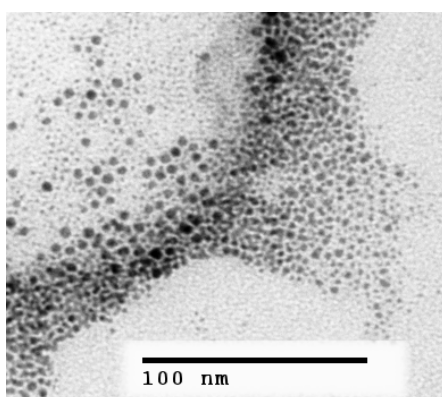
Nanoparticle size obtained by TEM: 4 ± 2.3 (≈ 0.3 amines *per* alcohol).

TEM micrographs and the corresponding size histograms of HFIP-AuNPs and their amine complexes:

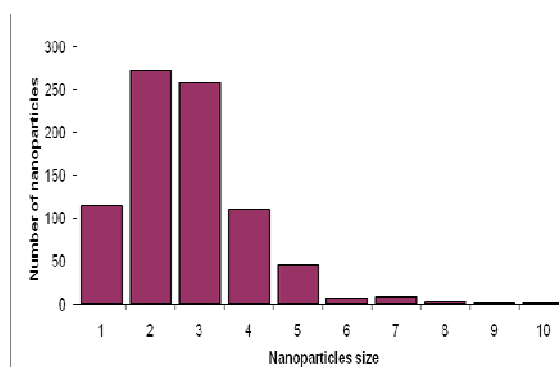
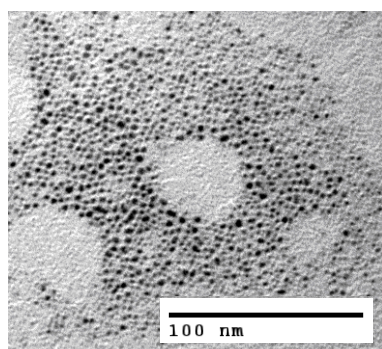
AuNPs: 2.8 ± 1.4 nm



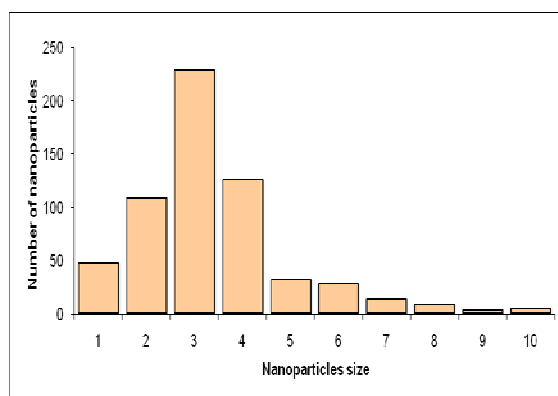
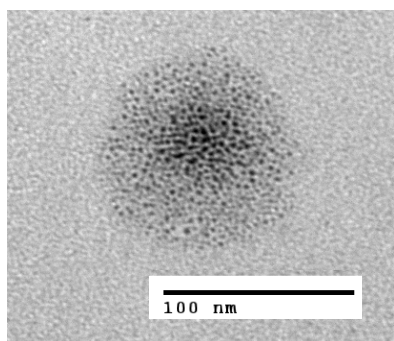
AuNPs-piperazine: 2.8 ± 1.9 nm



AuNPs-DABCO: 2.8 ± 1.3 nm



AuNPs-TBA: 2.9 ± 1.6 nm



AuNPs-TDA: 4.0 ± 2.3 nm

