

Ultrasmall NHC-coated Gold Nanoparticles Obtained through Solvent Free Thermolysis of Organometallic Au(I) Complexes

Julian Crespo,^a Yannick Guari,^{*b} Alfonso Ibarra,^c Joulia Larionova,^b Tania Lasanta,^a Danielle Laurencin,^b José M. López-de-Luzuriaga,^a Miguel Monge,^{*a} M. Elena Olmos^a and Sébastien Richeter^b

ELECTRONIC SUPPLEMENTARY INFORMATION

Experimental section

General

Compounds $[\text{Au}_2\text{Ag}_2(\text{C}_6\text{F}_5)_4(\text{OEt}_2)_2]_n$ and $[\text{Au}(\text{C}_6\text{F}_5)(\text{tht})]$ (tht = tetrahydrothiophene) were synthesized by standard procedures reported in the literature.^{1,2} $[\text{C}_{18}\text{MIM}]\text{Cl}$ was synthesized according to previously published procedures.³ $\text{Ti}(\text{acac})$ (acac^- = acetylacetonate), 3-aminopropyl functionalized silica, 4-nitrophenol and sodium borohydride were purchased from Sigma-Aldrich and used as received. All experiments for the preparation of the organometallic Au(I) precursors have been conducted under Ar using standard Schlenk techniques. Solvents were obtained from a solvent purification system (M-BRAUN MB SPS-800). All the synthetic approaches for ultrasmall nanoparticle synthesis described here have been repeated at least twice in order to ensure the reproducibility of the preparation methodology.

Instrumentation

The NMR spectra were recorded with a Bruker DPX300 and a Bruker Avance 400 spectrometers in CDCl_3 or d_8 -toluene solutions. Chemical shifts are expressed relative to CFCl_3 (^{19}F external). UV/Vis spectra were recorded with an Agilent 8453 Diode Array UV-visible spectrophotometer. Infrared spectra were recorded in the 4000-225 cm^{-1} range on a Nicolet Nexus FT-IR spectrophotometer, using Nujol mulls between polyethylene sheets. C, H analyses were carried out with a Perkin-Elmer 240C microanalyzer. Mass spectra were recorded on a Microflex MALDI-TOF Bruker spectrometer using dithranol as matrix. Samples for Transmission Electron Microscopy (TEM) were directly drop-casted from the crude toluene colloidal solution (2-3 drops) to carbon-coated Cu grids. The TEM images were obtained with a JEOL 2100 and with a FEI Cs image-corrected microscope operated at 300 kV at the Advanced Microscopy Laboratory (LMA), Instituto Universitario de Nanociencia de Aragon (INA), Zaragoza, Spain.

Synthesis of $[\text{C}_{18}\text{H}_{37}\text{MIM}][\text{Au}(\text{C}_6\text{F}_5)_2]$ (1): To a solution of $[\text{Au}_2\text{Ag}_2(\text{C}_6\text{F}_5)_4(\text{Et}_2\text{O})_2]$ (0.350 g, 0.274 mmol) in THF (30 mL), $\text{C}_{18}\text{H}_{37}\text{MIMCl}$ (0.203 g, 0.547 mmol) was added. The reaction mixture was stirred for 5 hours at room temperature and the white solid formed (AgCl) was filtered-off. The solvent was concentrated to ca. 5 mL under

vacuum and complex **1** was obtained by precipitation with *n*-hexane. Crystals suitable for X-ray diffraction analysis of **1** were grown by slow diffusion of *n*-hexane in a saturated CH₂Cl₂ solution of complex **1**. Yield: (95 %). Anal. Calcd for C₃₄H₄₃AuF₁₀N₂: C 47.12 %, H 5.00 %, N 3.23 %. Found: C, 46.98%, H 4.95%, N 3.13. IR ν (Au-C₆F₅) at 1500, 954 and 786 cm⁻¹. MALDI-TOF(-): *m/z* = 531 (100%) [Au(C₆F₅)₂]⁻; MALDI(+): *m/z* = 335 (100%) [C₁₈H₃₇MIM]⁺. ¹H NMR (CDCl₃, 400MHz, 294 K): 0.84 (t, 3H, **CH**₃); 1.15-1.35 (m, 30H, **-CH**₂-), 1.78 (m, 2H, NH₂-CH₂-**CH**₂-), 3.98 (s, 3H, N-**CH**₃), 4.11 (t, 2H, N-**CH**₂), 7.15 (s, 2H, N-**CH=CH**-N), 8.89 ppm (s, 1H, N-**CH**-N). ¹⁹F NMR: -116.3 (dd, 4 F, **F**_o); -160.7 (t, 2 F, **F**_p, ³J_{F-F}=20 Hz), d -162.9 (m, 4 F, **F**_m). Melting point: 85.2 °C

Synthesis of [C₁₈H₃₇MIM][Au(C₆F₅)Cl] (2): To a solution of [Au(C₆F₅)(tht)] (0.200 g, 0.442 mmol) in CH₂Cl₂ (30 mL), C₁₈H₃₇MIMCl (0.164 g, 0.442 mmol) was added and the reaction mixture was stirred for 30 minutes. Then the solution was concentrated under vacuum and complex **2** was precipitated with *n*-hexane. Yield: 96%. Anal. Calcd for C₂₈H₄₃AuClF₅N₂: C 45.75%, H 5.87%, N 4.13. Found: C 45.70%, H 5.87%, N 4.13%. IR ν (Au-C₆F₅) at 1508, 952 and 805 cm⁻¹. MALDI-TOF(-): *m/z* = 399 (75%) [Au(C₆F₅)Cl]⁻; *m/z* = 531 (25%) [Au(C₆F₅)₂]⁻; MALDI(+): *m/z* = 335 (100%) [C₁₈H₃₇MIM]⁺. ¹H NMR (CDCl₃, 400MHz, 294 K): 0.84 (t, 3H, **CH**₃); 1.10-1.35 (m, 30H, **-CH**₂-), 1.88 (m, 2H, NH₂-CH₂-**CH**₂-), 4.05 (s, 3H, N-**CH**₃), 4.24 (t, 2H, N-**CH**₂), 7.26 (s, 2H, N-**CH=CH**-N), 9.30 ppm (s, 1H, N-**CH**-N). ¹⁹F NMR: -116.5 (dd, 4 F, **F**_o); -161.2 (t, 2 F, **F**_p, ³J_{F-F}=20 Hz), d -163.3 (m, 4 F, **F**_m).

Synthesis of [Au(C₆F₅)(NHC-C₁₈H₃₇)] (3): To a solution of [Au(C₆F₅)Cl][C₁₈MIM] (0.200 g, 0.272 mmol) in CH₂Cl₂ (30 mL), Tl(acac) (0.099 g, 0.327 mmol) was added and the mixture was stirred at room temperature. After 3 h of reaction the white solid (TlCl) was filtered-off and the solution was concentrated under vacuum to ca. 5 mL. Complex **3** was obtained by precipitation with *n*-hexane. Alternatively, complex **3** can be obtained by refluxing at 110 °C a toluene solution of [C₁₈H₃₇MIM][Au(C₆F₅)₂] (**1**) (0.200 g, 0.230 mmol). After 4 h of reflux the reaction was stopped. Evaporation of the solvent to ca. 5 mL and addition of *n*-hexane gave rise to complex **3** as a white solid.

Yield: (93%). Anal. Calcd for C₂₈H₄₃AuF₅N₂: C 48.18%, H 6.06%, N 4.01. Found: C 47.88%, H 6.06%, N 3.99%. IR ν (Au-C₆F₅) at 1500, 954 and 787 cm⁻¹. MALDI-TOF(-): *m/z* = 531 (100%) [Au(C₆F₅)₂]⁻; MALDI(+): *m/z* = 335 (100%) [C₁₈H₃₇MIM]⁺. ¹H NMR (CDCl₃, 400MHz, 294 K): 0.87 (t, 3H, **CH**₃); 1.13-1.42 (m, 30H, **-CH**₂-), 1.88

(m, 2H, NH₂-CH₂-CH₂-), 3.90 (s, 3H, N-CH₃), 4.20 (t, 2H, N-CH₂), 6.93 (s, 2H, N-CH=CH-N). ¹⁹F NMR: -116.2 (dd, 4 F, F_o); -160.1 (t, 2 F, F_p, ³J_{F-F}=20 Hz), d -163.2 (m, 4 F, F_m). Melting point: 81.6 °C

Synthesis of Au UNPs (1a): Complex [C₁₈H₃₇MIM][Au(C₆F₅)₂] (**1**) (0.020 g, 0.023 mmol) was placed in a sealed tube and heated at 285°C for 10 min. The residue consisted of a dark brown solid. TEM and UV/Vis samples were prepared by dissolution of the solid in dichloromethane.

Synthesis of Au UNPs (3a): Complex [Au(C₆F₅)(NHC-C₁₈H₃₇)] (0.020 g, 0.029 mmol) was placed in a sealed tube and heated at 285°C for 3 min. The residue consisted of a black solid with metallic lustre. TEM and UV/Vis samples were prepared by dissolution of the solid in dichloromethane. Analysis expected for a 1:1 NHC-C₁₈H₃₇:Au molar ratio: 49,69 %C 7,96 %H 5,26 %N. Found: 48,29 %C 7,14 %H 5,16 %N.

Synthesis of Au UNPs (3b): Complex [Au(C₆F₅)(NHC-C₁₈H₃₇)] (0.020 g, 0.029 mmol) was placed in a sealed tube and heated at 250°C for 30 min. The residue consisted of a black solid with metallic lustre. TEM and UV/Vis samples were prepared by dissolution of the solid in dichloromethane.

Synthesis of NHC-Au-UNPs-SiO₂ nanocomposite material: Au UNPs (**3a**) (0.203 g) were dissolved in a round-bottom flask using dichloromethane (30 mL) and 3-aminopropyl functionalized silica (0.435 g) was added. After 6 h of stirring the mixture was centrifuged and washed with acetone several times. The obtained solid was filtered-off and dried under vacuum leading to nanomaterial (**4**) as a brown solid. A sample for TEM was prepared by addition of several drops of a dispersion of **4** in dichloromethane.

Crystal structure determination of complex 1

Single crystals of complex **1** were mounted in mineral oil on a glass fiber and transferred to the cold stream of a Nonius Kappa CCD diffractometer equipped with an Oxford Instruments low-temperature attachment. Data were collected by monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) with scan types ω and ϕ and semiempirical absorption correction (based on multiple scans). The structures were solved by direct methods and refined on F^2 using SHELXL-97.⁴ All non-hydrogen atoms were anisotropically refined and hydrogen atoms were included using a riding model.

¹³C solid state NMR experiments

Solid state NMR experiments were performed on a Varian VNMRS 600 MHz (14.1 T) NMR spectrometer, using a 1.6 mm Varian T3 HXY MAS probe. The operating

frequency for ^{13}C was 150.83, 192.44. Temperature regulation was used during the experiments, to avoid any heating of the sample over 25°C during the spinning.

^1H - ^{13}C CPMAS NMR spectra were recorded spinning at 25 kHz, using a contact time of 2.5 ms (ramped pulse), and 100 kHz spinal-64 ^1H decoupling during acquisition. The recycle delays ranged from 0.8 to 8 s, and the number of transients acquired from 2000 to 8000. ^{13}C chemical shifts were referenced externally to adamantane (used as a secondary reference), the high frequency peak being set to 38.5 ppm.

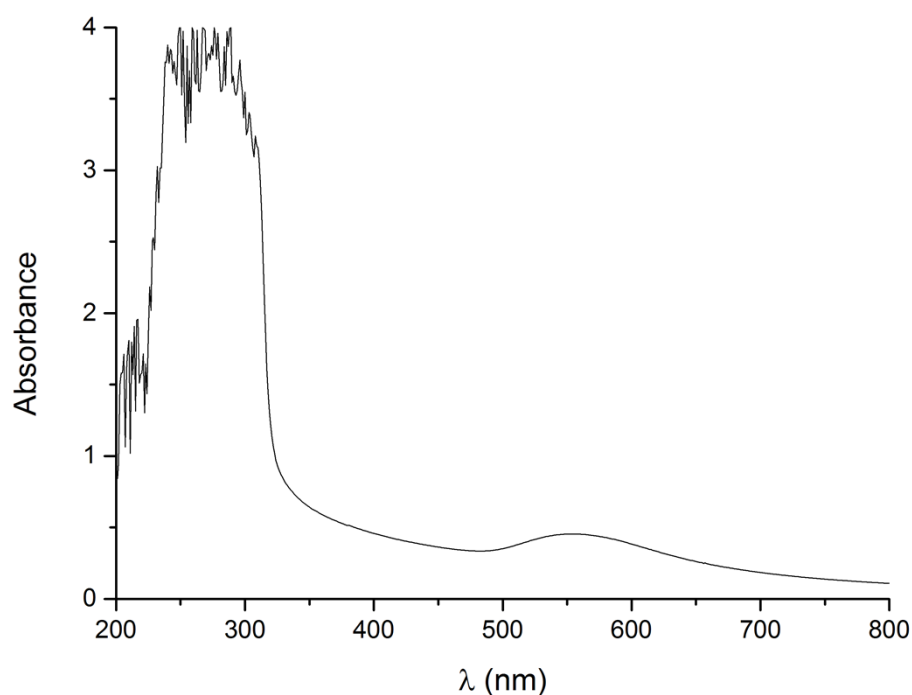


Fig S1. UV-Vis spectrum of Au UNPs **1a** in dichloromethane.

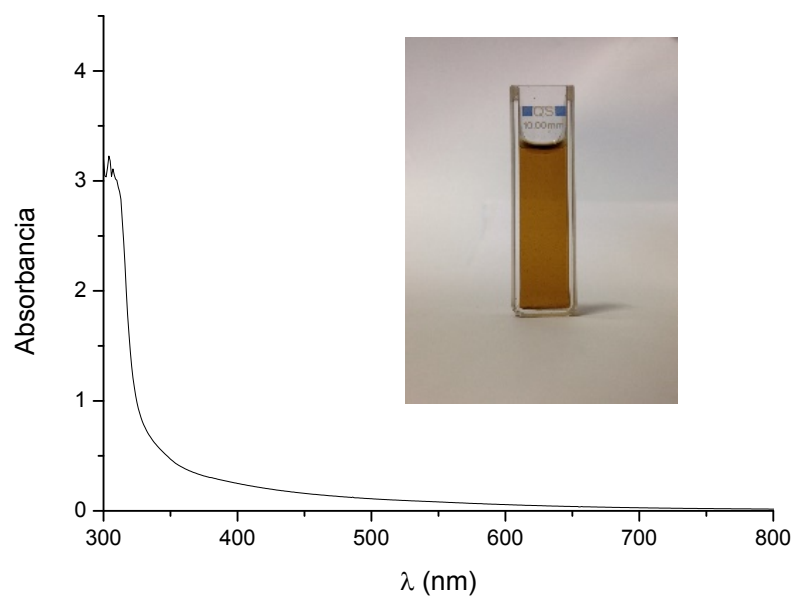


Fig S2. UV-Vis spectrum of Au UNPs **3a** in dichloromethane as solvent.

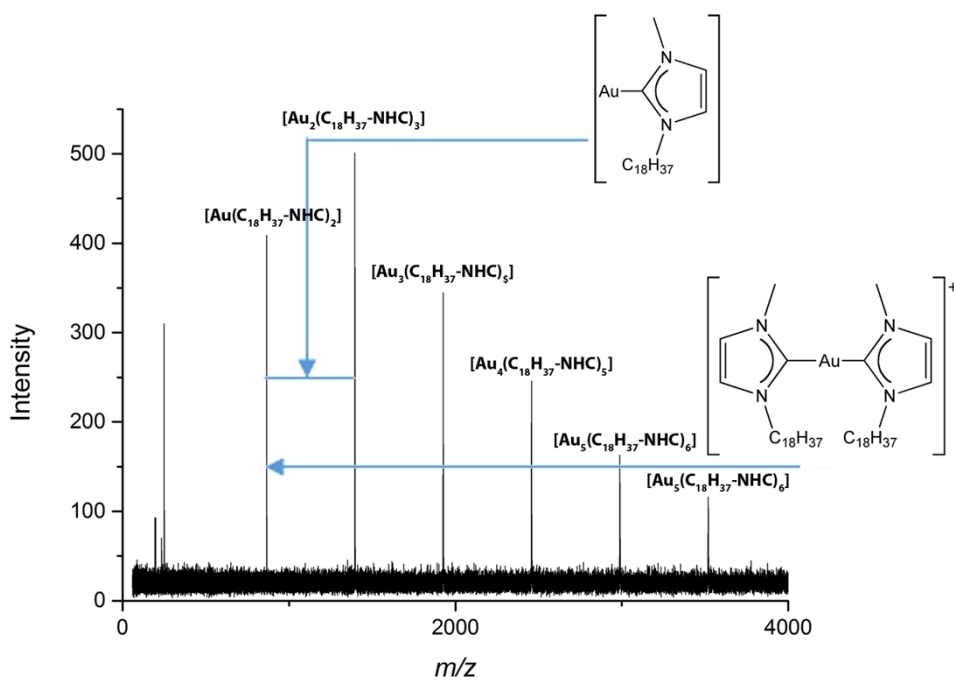


Fig S3. MALDI-TOF(+) spectrum of Au UNPs **3a**

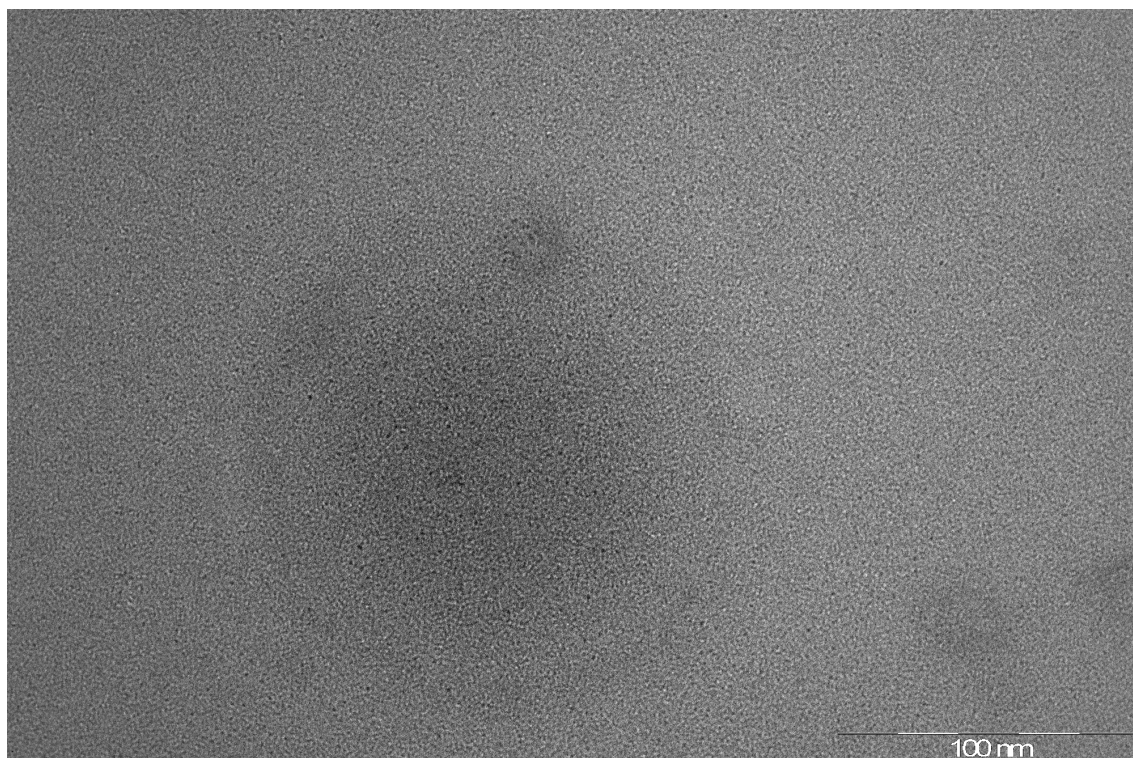


Fig S4. Panoramic TEM image of Au UNPs **3a** formed upon thermolysis of complex **3** during 3 min at 285 °C.

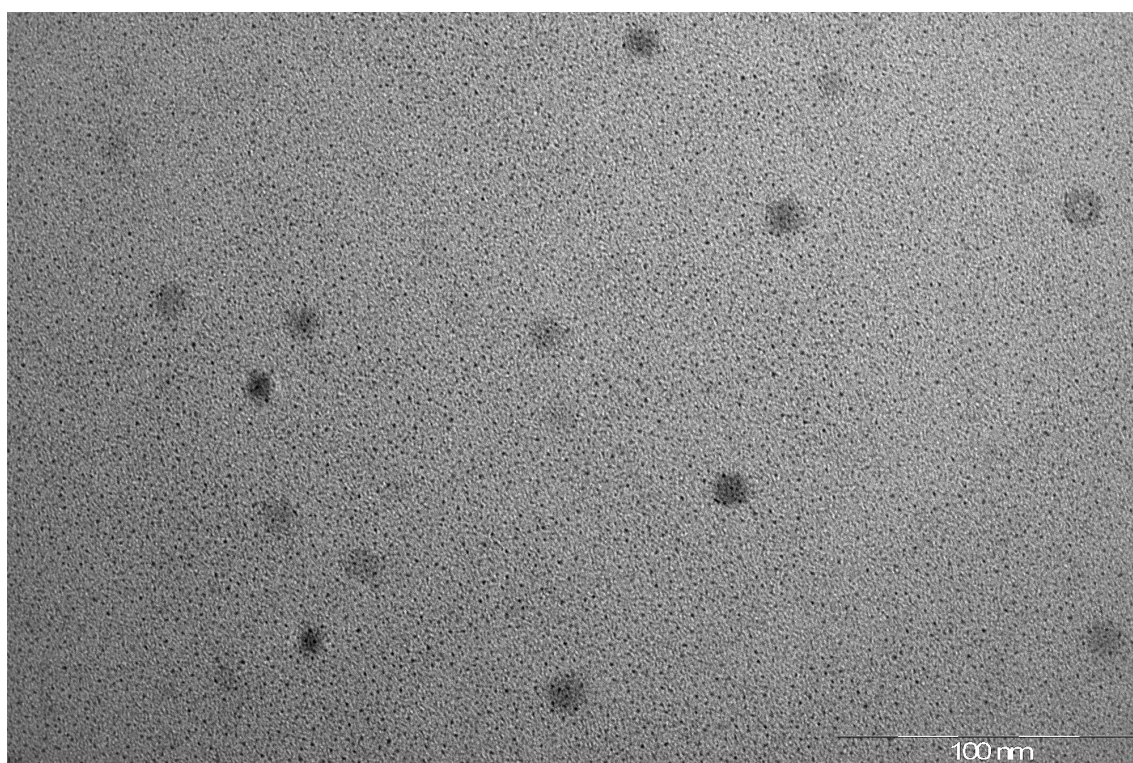


Fig S5. Panoramic TEM image of Au UNPs **3b** formed upon thermolysis of complex **3** during 30 min at 250 °C.

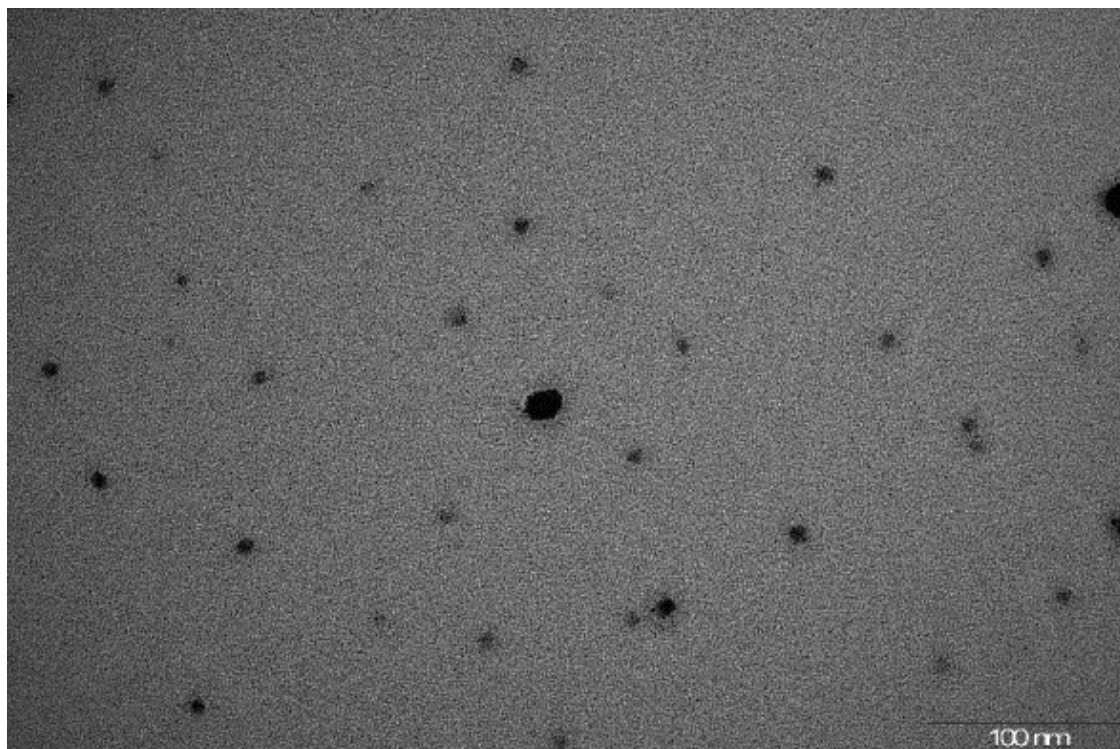


Fig S6. Panoramic TEM image of Au UNPs **3b** formed upon thermolysis of complex **3** during 60 min at 250 °C.

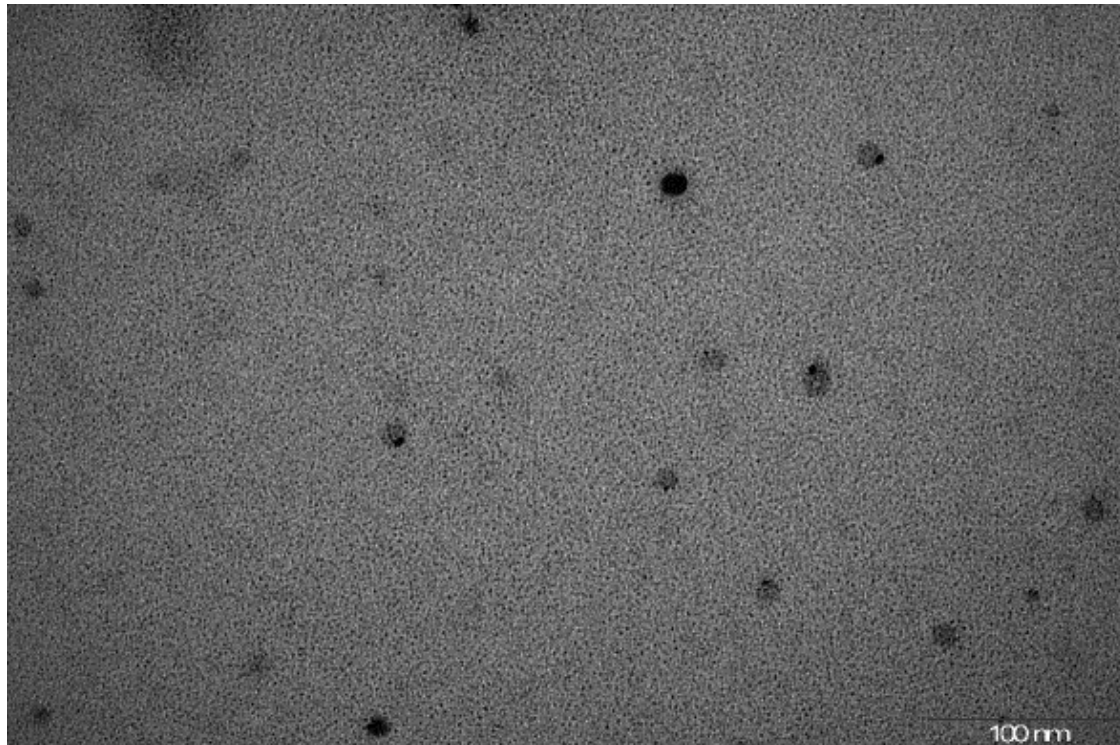


Fig S7. Panoramic TEM images of Au UNPs **3b** formed upon thermolysis of complex **3** during 180 min at 250 °C.

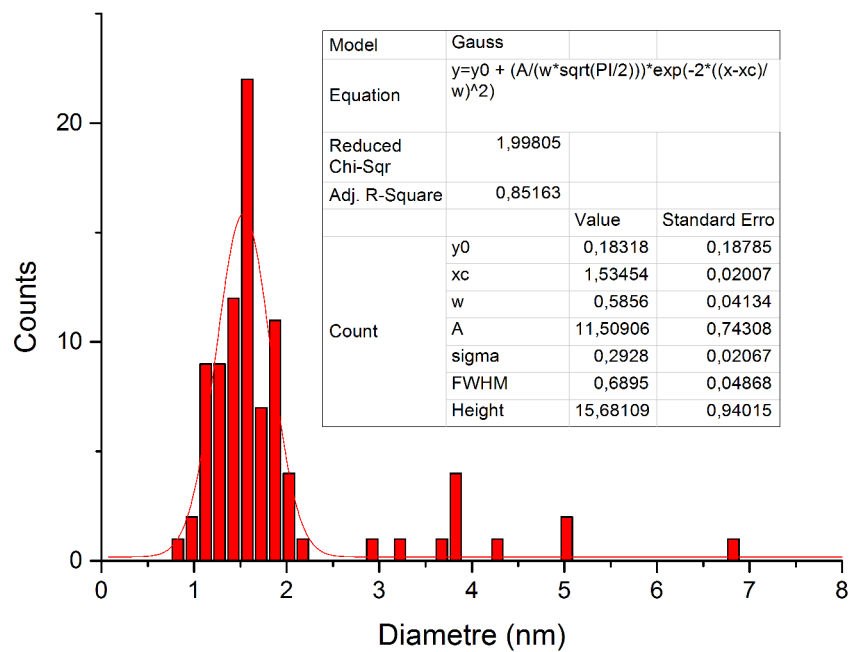


Fig S8. Size histogram of Au UNPs **1a**.

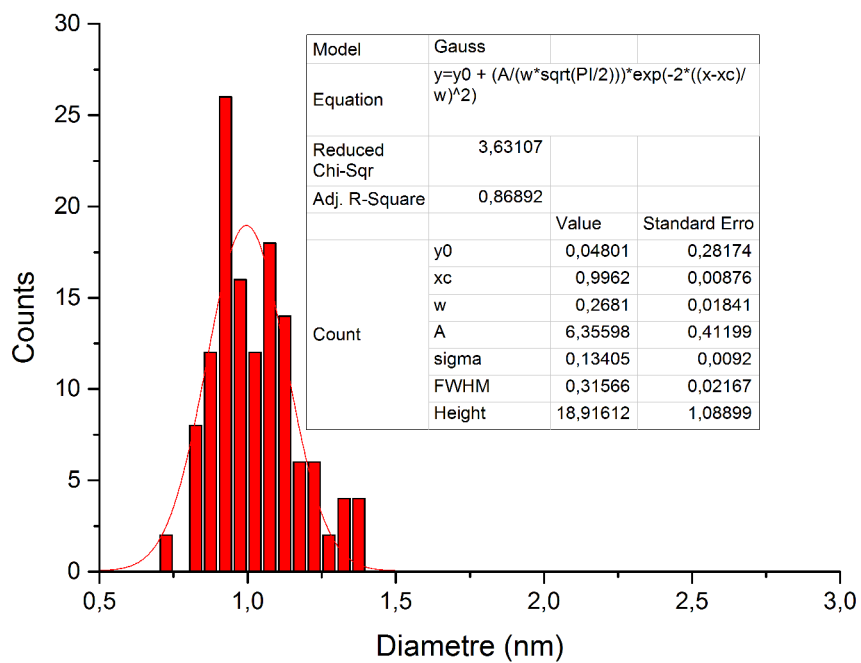


Fig S9. Size histogram of Au UNPs **3a**.

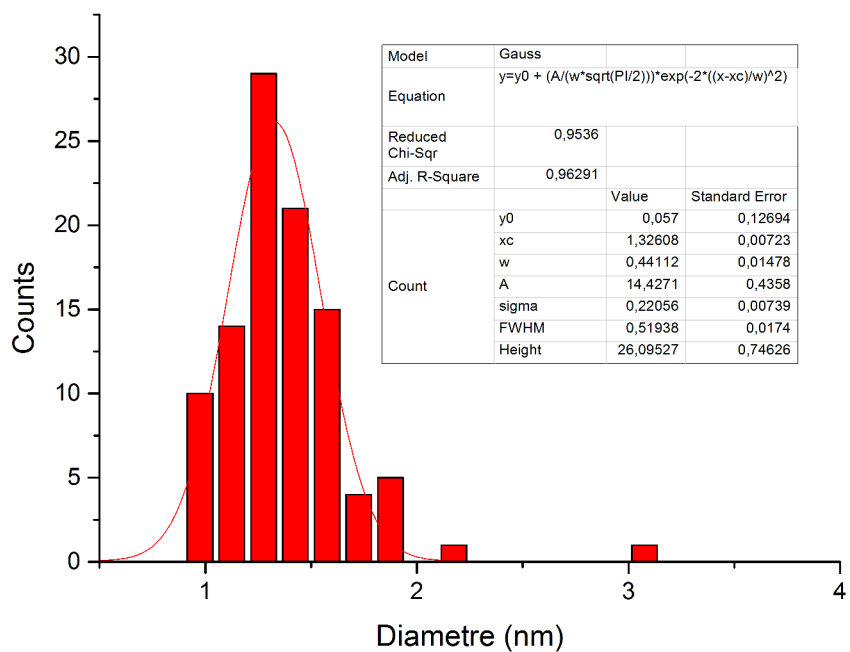


Fig S10. Size histogram of Au UNPs **3b**.

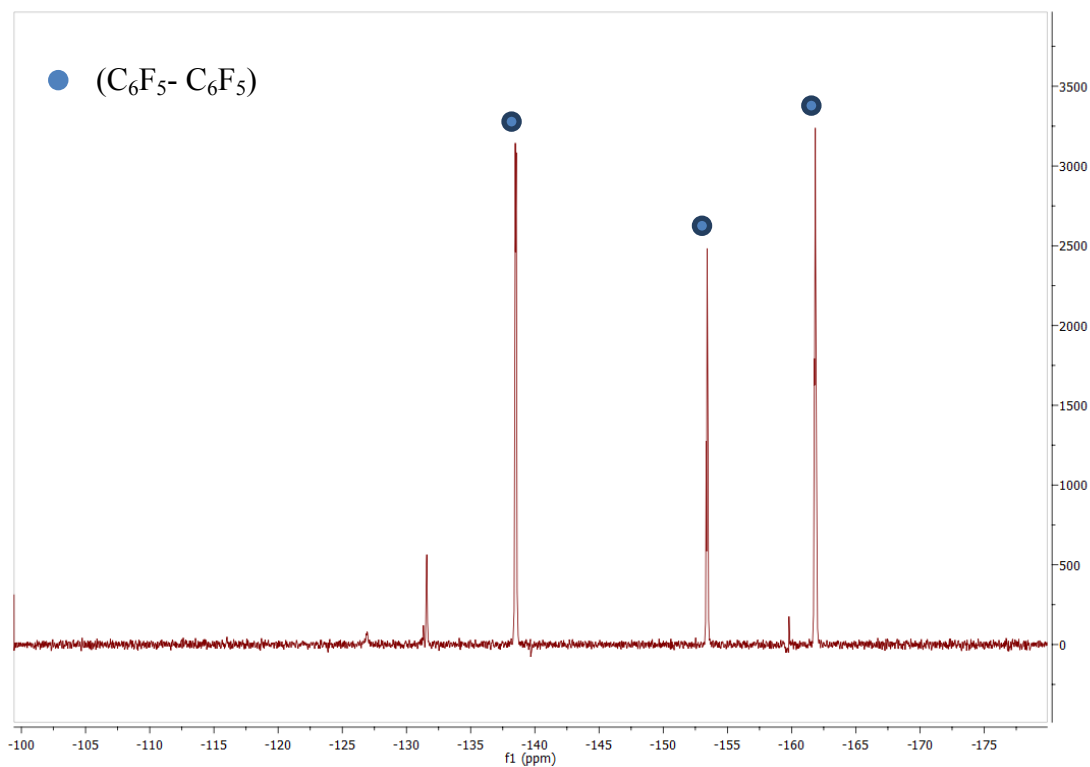


Fig S11. ¹⁹F NMR spectrum in CDCl₃ of the crude reaction mixture upon thermolysis of complex **3** after 3 min.

Catalytic test:

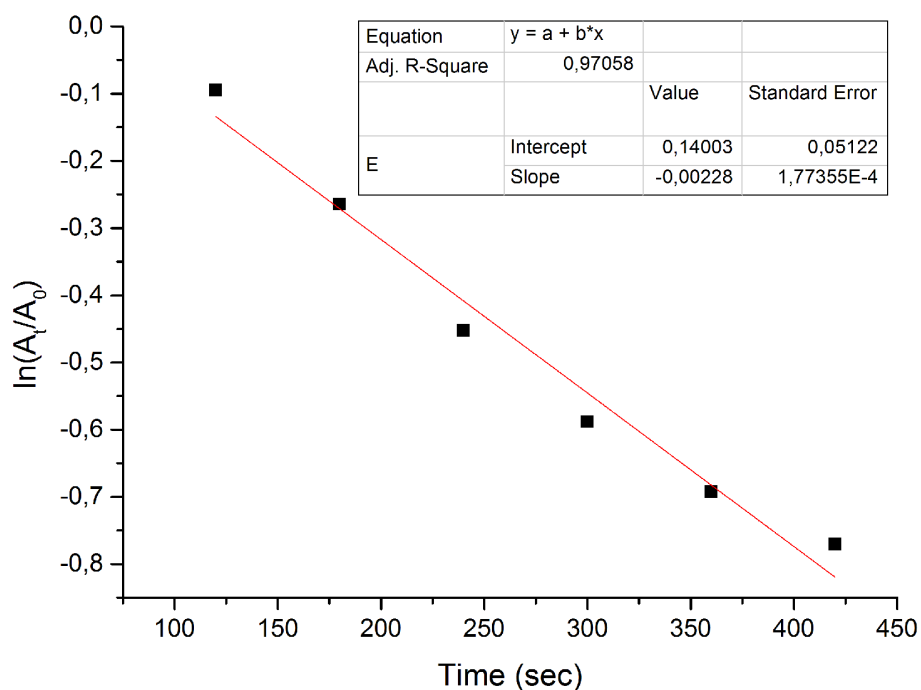


Fig S14. Plot of $\ln(A_t/A_0)$ vs time (sec) and linear fit. (A_t : absorbance at time t; A_0 : absorbance at time = 0) showing a pseudo-first order kinetics.

References

- (1) E. J. Fernández, M. C. Gimeno, A. Laguna, J. M. López-de-Luzuriaga, M. Monge, P. Pyykkö, D. Sundholm, *J. Am. Chem. Soc.* 2000, **122**, 7287.
- (2) R. Usón, A. Laguna, J. Vicente, *J. Chem. Soc. Chemical Communications* 1976, 353.
- (3) Adapted procedure from Y. Zhou, M. Antonietti, *Chem. Mater.* 2004, **16**, 540.
- (4) G. M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997.