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

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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 \([\text{Au}(\text{C}_6\text{F}_5)\text{(tht)}]\) (tth = 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.\(^3\) \(\text{Ti(acac)} \) (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 d8-toluene solutions. Chemical shifts are expressed relative to CFCl\(_3\) \((^{19}\text{F external})\). 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 \([\text{Au}_2\text{Ag}_2\text{(C}_6\text{F}_5)_4\text{(OEt}_2)_2]_n\) (0.350 g, 0.274 mmol) in THF (30 mL), \([\text{C}_{18}\text{H}_{37}\text{MIM}]\text{Cl}\) (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 \textit{n}-hexane. Crystals suitable for X-ray diffraction analysis of 1 were grown by slow diffusion of \textit{n}-hexane in a saturated CH\textsubscript{2}Cl\textsubscript{2} solution of complex 1. Yield: (95\%). Anal. Calcd for C\textsubscript{34}H\textsubscript{43}AuF\textsubscript{10}N\textsubscript{2}: C 47.12 \%, H 5.00 \%, N 3.23 \%. Found: C, 46.98\%, H 4.95\%, N 3.13. IR ν(Au-C\textsubscript{6}F\textsubscript{5}) at 1500, 954 and 786 cm\textsuperscript{-1}. MALDI-TOF(-): m/z = 531 (100\%) [Au(C\textsubscript{6}F\textsubscript{5})\textsubscript{2}]\textsuperscript{-}; MALDI(+): m/z = 335 (100\%) [C\textsubscript{18}H\textsubscript{37}MIM]\textsuperscript{+}. \textit{^1}H NMR (CDCl\textsubscript{3}, 400MHz, 294 K): 0.84 (t, 3H, CH\textsubscript{3}); 1.15-1.35 (m, 30H, -CH\textsubscript{2}-), 1.78 (m, 2H, NH\textsubscript{2}-CH\textsubscript{2}-CH\textsubscript{2}-), 3.98 (s, 3H, N-CH\textsubscript{3}), 4.11 (t, 2H, N-CH\textsubscript{2}), 7.15 (s, 2H, N-CH=CH-N), 8.89 ppm (s, 1H, N-CH-N).

Synthesis of [C\textsubscript{18}H\textsubscript{37}MIM][Au(C\textsubscript{6}F\textsubscript{5})Cl] (2): To a solution of [Au(C\textsubscript{6}F\textsubscript{5})(tht)] (0.200 g, 0.442 mmol) in CH\textsubscript{2}Cl\textsubscript{2} (30 mL), C\textsubscript{18}H\textsubscript{37}MIMCl (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 \textit{n}-hexane. Yield: 96\%. Anal. Calcd for C\textsubscript{28}H\textsubscript{43}AuClF\textsubscript{5}N\textsubscript{2}: C 45.75\%, H 5.87\%, N 4.13\%. IR ν(Au-C\textsubscript{6}F\textsubscript{5}) at 1508, 952 and 805 cm\textsuperscript{-1}. MALDI-TOF(-): m/z = 399 (75\%) \[\text{Au(C}_6\text{F}_5\text{)Cl}\]; MALDI(+): m/z = 531 (100\%) [Au(C\textsubscript{6}F\textsubscript{5})\textsubscript{2}]\textsuperscript{-}; MALDI(+): m/z = 399 (75\%) \[\text{Au(C}_6\text{F}_5\text{)Cl}\]; MALDI(+): m/z = 531 (100\%) [Au(C\textsubscript{6}F\textsubscript{5})\textsubscript{2}]\textsuperscript{-}. 1\textit{H} NMR (CDCl\textsubscript{3}, 400MHz, 294 K): 0.84 (t, 3H, CH\textsubscript{3}); 1.10-1.35 (m, 30H, -CH\textsubscript{2}-), 1.88 (m, 2H, NH\textsubscript{2}-CH\textsubscript{2}-CH\textsubscript{2}-), 4.05 (s, 3H, N-CH\textsubscript{3}), 4.24 (t, 2H, N-CH\textsubscript{2}), 7.26 (s, 2H, N-CH=CH-N), 9.30 ppm (s, 1H, N-CH-N). \textsuperscript{19}F NMR: -116.5 (dd, 4 F, F\textsubscript{o}); -161.2 (t, 2 F, F\textsubscript{p}, \textsuperscript{3}J_{F-F}=20 Hz), d -163.3 (m, 4 F, F\textsubscript{m}).

Melting point: 85.2 °C

Synthesis of [Au(C\textsubscript{6}F\textsubscript{5})(NHC-C\textsubscript{18}H\textsubscript{37})] (3): To a solution of [Au(C\textsubscript{6}F\textsubscript{5})Cl][C\textsubscript{18}MIM] (0.200 g, 0.272 mmol) in CH\textsubscript{2}Cl\textsubscript{2} (30 mL), Ti(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 \textit{n}-hexane. Alternatively, complex 3 can be obtained by refluxing at 110 °C a toluene solution of [C\textsubscript{18}H\textsubscript{37}MIM][Au(C\textsubscript{6}F\textsubscript{5})\textsubscript{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 \textit{n}-hexane gave rise to complex 3 as a white solid. Yield: (93\%). Anal. Calcd for C\textsubscript{28}H\textsubscript{43}AuF\textsubscript{5}N\textsubscript{2}: C 48.18\%, H 6.06\%, N 4.01. Found: C 47.88\%, H 6.06\%, N 3.99\%. IR ν(Au-C\textsubscript{6}F\textsubscript{5}) at 1500, 954 and 787 cm\textsuperscript{-1}. MALDI-TOF(-): m/z = 531 (100\%) [Au(C\textsubscript{6}F\textsubscript{5})\textsubscript{2}]\textsuperscript{-}; MALDI(+): m/z = 335 (100\%) [C\textsubscript{18}H\textsubscript{37}MIM]\textsuperscript{+}. \textit{^1}H NMR (CDCl\textsubscript{3}, 400MHz, 294 K): 0.87 (t, 3H, CH\textsubscript{3}); 1.13-1.42 (m, 30H, -CH\textsubscript{2}-), 1.88 (m, 2H, NH\textsubscript{2}-CH\textsubscript{2}-CH\textsubscript{2}-), 4.05 (s, 3H, N-CH\textsubscript{3}), 4.24 (t, 2H, N-CH\textsubscript{2}), 7.26 (s, 2H, N-CH=CH-N), 9.30 ppm (s, 1H, N-CH-N). \textsuperscript{19}F NMR: -116.5 (dd, 4 F, F\textsubscript{o}); -161.2 (t, 2 F, F\textsubscript{p}, \textsuperscript{3}J_{F-F}=20 Hz), d -163.3 (m, 4 F, F\textsubscript{m}).
Synthesis of Au UNPs (1a): Complex \([\text{C}_{18}\text{H}_{37}\text{MIM}]\text{[Au(C}_6\text{F}_{5})_2]\) (1) (0.020 g, 0.023 mmol) was placed in a sealed tube and heated at 285ºC 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 \([\text{Au(C}_6\text{F}_{5})(\text{NHC-C}_{18}\text{H}_{37})]\) (0.020 g, 0.029 mmol) was placed in a sealed tube and heated at 285ºC 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-C\(_{18}\text{H}_{37}:\text{Au}\) 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 \([\text{Au(C}_6\text{F}_{5})(\text{NHC-C}_{18}\text{H}_{37})]\) (0.020 g, 0.029 mmol) was placed in a sealed tube and heated at 250ºC 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-SiO\(_2\) 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 Kα radiation (\(\lambda = 0.71073\) Å) with scan types \(\omega\) and \(\phi\) 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.

\(^{13}\text{C} \text{solid state NMR experiments}\)

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 $^{13}\text{C}$ 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.

$^{1}\text{H}-^{13}\text{C}$ CPMAS NMR spectra were recorded spinning at 25 kHz, using a contact time of 2.5 ms (ramped pulse), and 100 kHz spinal-64 $^{1}\text{H}$ decoupling during acquisition. The recycle delays ranged from 0.8 to 8 s, and the number of transients acquired from 2000 to 8000. $^{13}\text{C}$ 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.

![Size histogram of Au UNPs 3b.](image)

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<td>Equation</td>
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| Reduced Chi-Sqr | 0.9530 |
| Adj. R-Square | 0.96291 |

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Fig S11. 19F NMR spectrum in CDCl$_3$ of the crude reaction mixture upon thermolysis of complex 3 after 3 min.

![19F NMR spectrum in CDCl$_3$.](image)
Fig S12. $^1$H NMR spectrum of complexes 1 and 3 and Au UNPs (1a).

Fig S13. $^1$H NMR spectrum of complex 3 and Au UNPs (3a).
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