Electronic Supplementary Material (ESI)

Size controled formation of Ag nanoparticles by direct bonding of Ruthenium complexes bearing a terminal mono- or bi-pyridil group.

Cédric R. Mayer,*[a] Eddy Dumas[a] and Francis Sécheresse
[a] UMR CNRS 8637, IREM, Institut Lavoisier, Université de Versailles Saint-Quentin, 45 Avenue des Etats-Unis, 78 035 Versailles.France. Fax: (+33)139254381; Tel: (+33)139254397; E-mail: cmayer@chimie.uvsq.fr

1- Experimental

All reagents and solvents were purchased from Aldrich and used as received. The 1,10-phenanthroline-5,6-dione (phen-dion) was synthesized following ref. 1 without modifications and with similar yield. – Energy dispersive spectrometry was performed with a PGT-IMIX-PC and visualization of gold nanoparticles was performed with a transmission electron microscope (TEM) (microscope JEOL 2010 UHR) in the " Centre Régional de Mesures Physiques " Paris 6 : a drop of an acetonitrile solution was deposited and dried on a grid. – UV/Vis spectra were recorded on CH_3CN-dissolved samples, using a Perkin Elmer UV/Vis/NIR lambda 19 PC scanning spectrophotometer. – ESI-MS measurements were carried out with a HP 5989B single quadrupole mass spectrometer equipped with an electrospray source from Analytica of Branford. The instrument was operated in the positive ion mode.

2- Synthesis of $[(Phen)_2RuL\text{-}pyr]^{2+}$ [1]

A solution of $[(Phen)_2RuPhen\text{-}dion]Cl_2$ (1 g, 1.35 mmol), NH_4OAc (2.1 g , 27 mmol) and 4-pyridinecarboxaldehyde (400 µL, 4.25 mmol) in acetic acid (14.7 M, 80 mL) was stirred at 120°C for 6 h and then cooled to room temperature. The solution was neutralized with concentrated aqueous ammoniac and 200 mL of deionised water was added. The product was precipitated by addition of concentrated aqueous NH_4PF_6 solution, filtrated, washed with water and dried with diethylether. Then, the pure product was dissolved in acetonitrile and slowly precipitated with diethylether. Yield 1.1 g, 78 % (Found: C, 47.91; H, 2.79; N, 10.43; Ru; 9.36. $C_{42}H_{26}F_{12}N_8OP_2Ru$ requires C, 48.06; H, 2.5; N, 10.67; Ru, 9.63 %). ESI-MS (positive ion mode): m/z 380, $[C_{42}H_{26}N_8ORu]^{2+}$ theoretical m/z 379.9 (monoisotopic ion).

3- Synthesis of $[(Phen)_2RuL\text{-}phen]^{2+}$ [2]

$[(Phen)_2RuL\text{-}phen]^{2+}$ was synthesized as $[(Bpy)_2RuL\text{-}phen]^{2+}$ in ref. 2 but by using $[(Phen)_2Ru(fmp)]^{2+}$ instead of $[(Bpy)Ru(fmp)]^{2+}$ (with "fmp" corresponding to 2-(4-formylphenyl)imidazo[4,5-*f*][1,10]phenanthroline and "L-phen" corresponding to 2,2'-*p*-phenylene(imidazo[4,5-*f*][1,10]phenanthroline)). Elemental analysis: Found: C, 52.9; H, 2.83; N, 13.15; Ru; 7.72. $C_{56}H_{34}F_{12}N_{12}P_2Ru$ requires C, 53.13; H, 2.71; N, 13.28; Ru, 7.98 %. ESI-MS (positive ion mode): m/z 488.2, $[C_{56}H_{34}N_{12}Ru]^{2+}$ theoretical m/z 488.0 (monoisotopic ion).

4- Synthesis of silver nanoparticles in the presence of [1] and [2]

The syntheses were similar for both ruthenium complexes [1] or [2]. Only the ratios [Ru]/$AgNO_3$ were different and summarized in Table 1. A typical synthesis, with a ratio [1]/$AgNO_3$ = 6: $AgNO_3$ (5 mg, 29.5 µmol) was dissolved in 20 mL of CH_3CN and [1] was added. Then, an aqueous solution of $NaBH_4$ (80 µL, 4M) was added dropwise over 20 mn and the mixture was stirred during one hour. This red brown colloidal solution was stable for one month as observed by UV-vis and TEM.

Table 1 Summary of masses and ratios for different experimental procedures.[a]

	$AgNO_3$ (mg)	[Ru] (mg)	CH_3CN (ml)	Sample
[Ru-Lpy] 1	5	15.4	20	1A
	5	5.1	20	1B
	5	3	20	1C
[Ru-Lphen] 2	5	18.6	20	2A
	5	6.2	20	2B
	5	3.7	20	2C

[a] for all synthesis the volume of aqueous solution of $NaBH_4$ (0.4 M) was identical (80 µl).

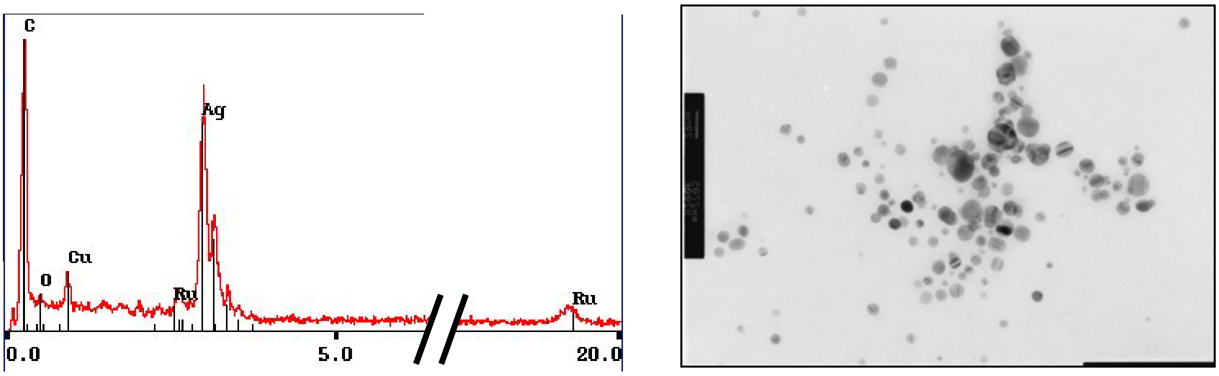

Figure S1. EDX of silver nanoparticles coated by complex 2 with the ratio Ag/[2] = 6 and TEM image of the region analyzed by EDX.

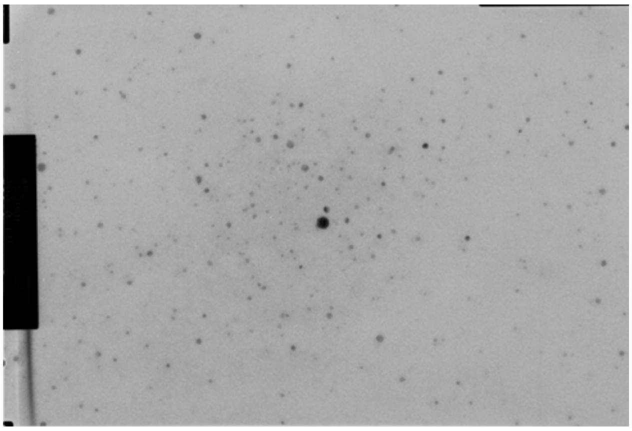

Figure S2. Tem image of silver nanoparticles coated by complex 2 with the ratio Ag/[2] = 2.

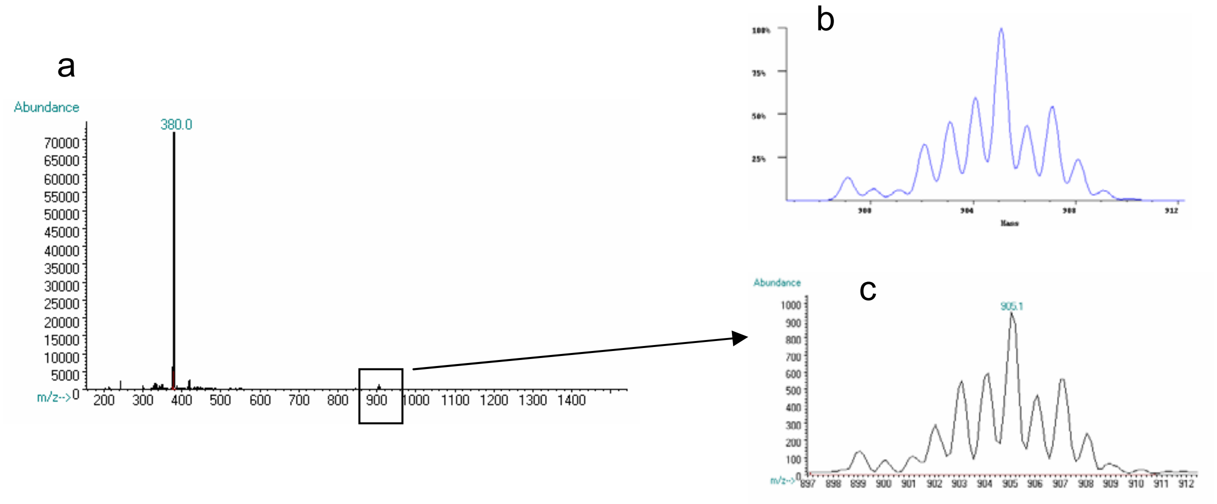

Figure S3. Mass spectrum of complex **1** (hexafluorophosphate salt) (a). Full spectrum, expansion of m/z = 905 with simulated spectrum for this monoisotopic ion $([2] + PF_6^-]^+)$ (b) and experimental spectrum (c).

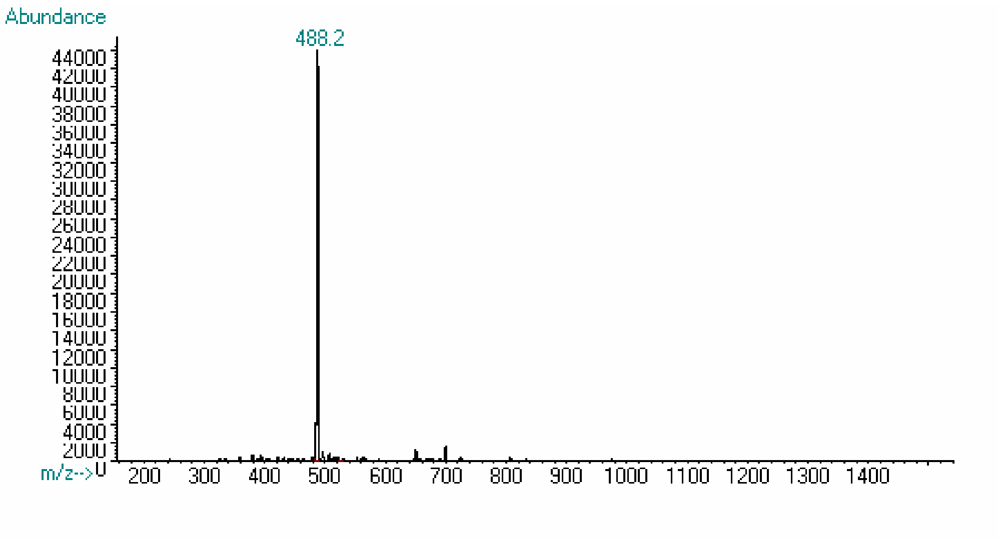

Figure S4. Mass spectrum of complex **2** (hexafluorophosphate salt).

Reference:

1 C. Hiort , P. Lincoln, B. Nordén, *J. Am . Chem. Soc.*, **1993**, 115, 3449.
2 H. Chao, R-H. Li, C-W. Jiang, H. Li, L-N. Ji and X-Y. Li, *J. Chem. Soc.Dalton Trans.*, 2001, 1920.