Size controlled formation of silver nanoparticles by direct bonding of ruthenium complexes bearing a terminal mono- or bi-pyridyl group†

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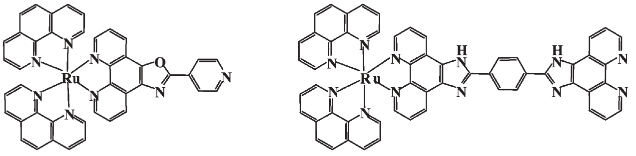
Two polypyridyl ruthenium complexes containing either a terminal pyridine or phenanthroline group have been used to coat silver nanoparticles and control their size depending on the Ag/[Ru^{II}] ratio.

Nanocomposite materials have been extensively studied in recent years, in particular systems including metallic nanoparticles such as platinum, silver or gold nanoparticles. Interest in such systems is motivated by their numerous applications covering a large field from DNA sequencing[1] to catalysis,[2] optics[3] and nanoscale electronics.[4] More specifically, the synthesis of functionalized silver particles has received considerable attention because of their relevance for antimicrobial applications, as a substrate for surface-enhanced Raman spectroscopy[5] and catalysis.

Parallel to this area, the chemistry of metallic complexes based on ruthenium(II) and polypyridyls itself constitutes a vast field of research with applications ranging from antitumor activity,[6] to electronic devices,[7] and non linear optic properties.[8] The use of such ruthenium(II) complexes in nanocomposite systems is very promising and should allow combination of properties of these molecular complexes with properties of metallic nanoparticles. Nevertheless, the formation of such hybrid composite systems with ruthenium(II) complexes requires an appropriate bipyridyl ligand to ensure a good coating of the particles and the stability of the colloidal suspension.

In our group, we recently investigated the formation of nanometric composites based on gold nanoparticles and inorganic systems such as polyoxometalate[9] or (oxo)thiometalate species.[10] Here, we present a new type of nanocomposite materials based on silver nanoparticles and ruthenium(II) complexes, with direct and strong interaction between these two inorganic moieties. The aim of this first work was to prepare stable colloidal solutions of silver nanoparticles and to control their size by means of the Ag/[Ru] ratio and the nature of the ruthenium(II) complexes. We also focused on the anchoring point with the metallic surface which is not ensured with a conventional thiol group but with a pyridine or bipyridine function. Very few examples described the interaction between gold nanoparticles and a pyridine group.[11] Both ruthenium(II) complexes presented in this article contain two phenanthroline ligands and only diverge by the third bidentate ligand. In complex **1**, the third diimine ligand, (4-pyridine)oxazolo[4,5-*f*]phenanthroline (L-pyr), could be described as one pyridine group connected to a phenanthroline unit through an oxazole function (Fig. 1, complex **1**). In complex **2** the third ligand, 2,2′-*p*-phenylenebis(imidazo[4,5-*f*][1,10]phenanthroline) (L-phen), has been previously described by L.-N. Ji and co-workers[12] and is built of two phenanthroline units linked in the *para*-position of a phenyl group through two imidazole functions (Fig. 1, complex **2**).



1 **2**

Fig. 1 Structures of ruthenium(II) complexes.

Complex **1** was obtained in very good yield by direct reaction of 4-pyridinecarboxaldehyde with [Ru(Phen)$_2$Phen-dione]Cl$_2$ in the presence of an excess of ammonium acetate, as illustrated in Fig. 2. Complex **2** was synthesized using the procedure described by L.-N. Ji and co-workers,[12] except that phenanthroline ligand was used instead of bipyridine ligand. Both complexes **1** and **2** were isolated as hexafluorophosphate salts to further allow the synthesis of coated silver nanoparticles in acetonitrile medium.

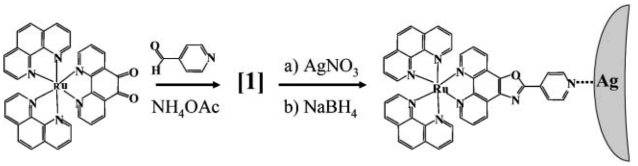


Fig. 2 Schematic route for the synthesis of nanoparticles coated with complex **1**.

The method used to functionalize silver nanoparticles is similar with both ruthenium complexes. AgNO$_3$ and **1** or **2** were dissolved in acetonitrile with different Ag/[Ru^{II}] ratios (2 to 10), in both cases the concentration in AgNO$_3$ (1.5 10^{-3} M) was identical. Then, the resulting red solution turned to red-brown with the progressive addition of an aqueous solution of NaBH$_4$ (0.4 M). For both complexes the colloidal solutions were stable for more than one month as confirmed by UV-vis and TEM analyses. A study of the influence of the Ag/[Ru^{II}] ratio revealed that only a small amount of metallic complex was necessary to efficiently coat the surface of the silver nanoparticles. This could be explained by the steric hindrance of the metallic complexes. For Ag/[Ru^{II}] ratios below 2,

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the TEM showed no evolution of the size of the particles. We also observed a spontaneous aggregation of reduced silver when the reduction occurs in the presence of complex containing no terminal pyridine function, like [(Phen)$_2$Ru(phenyl-imidazo[4,5-*f*][1,10]phenanthroline)]$^{2+}$ (with a terminal phenyl imidazole function instead of a terminal (4-pyridine-)oxazole function). A similar result was obtained using the complex [(Phen)$_2$Ru((4-cyano-)phenyl-imidazo[4,5-*f*][1,10]phenanthroline)]$^{2+}$. This is related to a weaker interaction between the electronic doublet of the nitrogen atom of a nitrile group and the silver surface than between the electronic doublet of a pyridine function and the silver nanoparticle.

Study of the influence of the nature of the ruthenium(II) compound only showed a change in the size of the nanoparticles obtained. While keeping the Ag/[Ru^{II}] ratio constant, smaller silver particles are obtained with complex **2**. With the ratio Ag/[Ru^{II}] = 2, monodisperse nanoparticles of 7–8 nm are observed with complex **1** while smaller monodisperse nanoparticles of 1–2 nm are obtained with complex **2**. By increasing this ratio, the size of the particles varies from about 20 nm for complex **1** to about 8 nm for complex **2** together with a higher polydispersity. Moreover, for **1**, using the ratio Ag/[Ru^{II}] = 10, the shape of the particle changes and the formation of few cylindrical particles, represented in Fig. 3b, is observed. These results confirm that the size of the nanoparticles can be controlled by the Ag/[Ru^{II}] ratio and illustrate the strong interaction between each complex and the surface of the nanoparticles. Indeed, the chelating bidentate phenanthroline groups ensure a stronger interaction with the metallic surface than the mono-pyridine groups. Probably due to this stronger interaction, the nanoparticles in formation are rapidly coated by complex **2**, and the growth of the nanoparticles is stopped. For all samples, EDS analysis of the particles observed by TEM revealed the presence of complex **1** or **2** around the colloids. This result indicates that, even if the particle/complex interactions are weaker with complex **1** than with complex **2**, both complexes ensure an effective coating of the nanoparticles and their stability in solution.

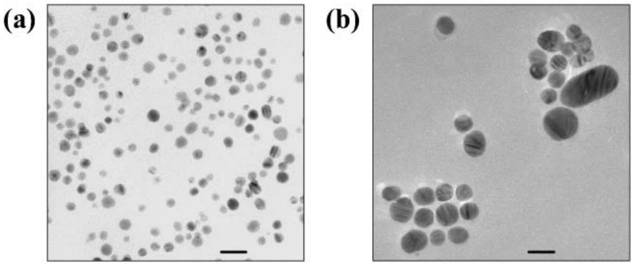

Fig. 3 TEM images of silver coated nanoparticles with the ratios Ag/[**1**] = 2 (a) and 10 (b). Scale: 20 nm.

UV-vis spectra were recorded between 250 and 800 nm. The spectrum of complex **1** (Fig. 4) consists of three bands at 263, 280 (shoulder) and 445 nm. Bands at 263 and 280 are attributed to the π–π intraligand transitions while the lowest and broader band at 445 is assigned to metal–ligand charge transfer (MLCT) and results of the overlapping of Ru(dπ) → L-pyr(π*) or Ru(dπ) → Phen(π*) transitions. The UV-vis spectrum of complex **2** is slightly different, showing four bands at 263, 280, 352 and 452 nm. This spectrum is similar to that described by L.-N. Ji *et al.* for [Ru(bpy)$_2$L-phen]$^{2+}$. By analogy, bands at 263, 280 and 352 are attributed to the π–π intraligand transitions while the lowest and broader band at 445 is assigned to MLCT. For both complexes two regions can be considered, region A corresponding to the π–π intraligand transitions and region B corresponding to MLCT. In all cases, the interaction of complexes with the surface of the nanoparticles is accompanied by a decrease of the absorption bands in region A and an increase of absorption in region B. Moreover, in the spectrum of **1**, for Ag/[Ru^{II}] ratios ranging from 6 to 10, an additional band is observed at 412 nm, corresponding to a surface plasmon (SP) band of silver particles since unprotected Ag particles are known to display an absorption band with a maximum at *ca.* 390 nm.[13] Here the shift of the SP band is attributed to a consequence of the strong interactions existing between silver particles and the ligands. The presence of the shifted SP band at *ca.* 412 nm provides clear evidence of the bonding of complex **1** *via* the pyridine group. This SP band is hardly detectable for Ag/[Ru^{II}] ratios below 6. This is probably due to the smaller size of the particles which therefore display a weaker absorbance, with a broader band, compared with the strong absorbance of the MLCT band. Moreover, for complex **2**, the polydispersity observed for Ag/[Ru^{II}] ratios above 6 contributes to the broadening of the band.[14]

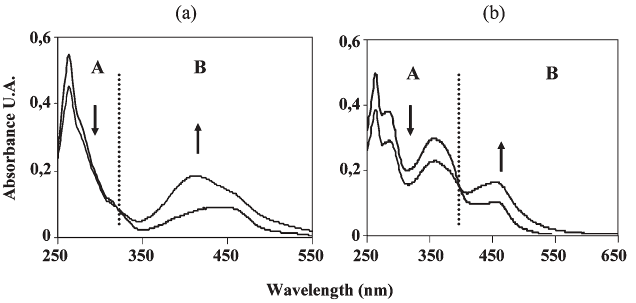

Fig. 4 Absorption spectra of (a) complex **1** before reduction (black line), complex **1** after reduction with silver particles for the ratio Ag/[**1**] = 6 (grey line), and (b) complex **2** before reduction (black line), complex **2** after reduction with silver particles for the ratio Ag/[**2**] = 6 (grey line).

In conclusion, we have presented here a new approach to efficiently coat ruthenium complexes on silver nanoparticles through a non-conventional group, using pyridine or bipyridine groups. In addition, similarly to the usual organothiols, we showed that it was possible to control the size of the nanoparticles through the Ag/[Ru^{II}] ratio and the nature of the ruthenium complex. We are currently studying the NLO properties of these ruthenium-coated silver nanoparticles to see the influence on the NLO responses of the direct interaction between the ruthenium complexes and the silver particles. This work will be extended to other metals such as gold or platinum, in other solvents and specifically in water (exchange of hexafluorophosphate by halides makes these particles soluble in water).

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