Gold nanocomposites with rigid fully conjugated heteroditopic ligands shell as nanobuilding blocks for coordination chemistry†

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Monodisperse and solvent adaptable gold nanoparticles stabilized by rigid and fully conjugated modified neocuproinium and terpyridinium salts have been characterized and further used as nanobuilding blocks for the synthesis of gold nanoparticles functionalized by polypyridyl ruthenium complexes.

Gold nanocomposites (Au-NCs) have been extensively studied owing to their unique tunable size- and shape-dependent optoelectronic properties.[1] The so-called Brust–Schiffrin method was decisive in this research area as it offered a straightforward and adaptable synthesis to obtain stable, rather monodisperse and easy to handle gold nanoparticles (Au-NPs).[2] The initial alkanethiol used by Brust and co-workers was later replaced by a variety of functionalizing agents of interest for applications such as catalysis, bio-sensing and nanotechnology.[1,3] Surprisingly, few examples of metallic complexes used as stabilizing agents have been described in the literature. Synergistic effects between the intrinsic properties of both the Au-NP and the metallic complexes could be expected for such nanocomposites. The metallic complexes were either interacting with the Au-NPs *via* electrostatic interactions,[4] or they were grafted onto the metallic surface *via* a thiol,[5] a dithiol,[6] or a dithiocarbamate terminated aliphatic chain.[7] Another approach was recently described in which Au-NPs functionalized by a variable chain length aliphatic thiol terminated by a terpyridine or a bipyridine group formed 3D aggregates in the presence of metallic ions.[8] To our knowledge, only three examples of metallic complexes grafted onto the surface of Au-NPs *via* a fully conjugated system have been described.[9,10]

Polypyridyl ruthenium complexes are well-known for their optical and electronic properties and for their interaction with DNA.[11] We recently reported the functionalization of silver nanoparticles by polypyridyl ruthenium complexes using a fully delocalized π-conjugated linker.[12] The fully conjugated bridge was used in order to facilitate potential electronic transfers between the ruthenium centre and the metallic NP.[10] In these systems, the connection between the ruthenium complex and the metallic surface was ensured by a pyridine or a phenanthroline group. While the strength of this connection was sufficient enough to ensure the stability of the NCs, partial desorption of the ruthenium complex was often observed, mainly when using a pyridine linker. Indeed, such desorption processes have to be efficiently overcome to maintain the stability of the colloidal solution, but also to avoid interference of the "free" ligands throughout physical measurements such as luminescence or electrochemical analysis. We therefore decided to develop a new strategy to graft the ruthenium complexes onto the Au-NPs to strengthen its interaction with the metallic surface, while maintaining the fully conjugated nature of the bridge. Here we report the synthesis of the two heteroditopic ligands (4-(2-mercaptopyridyl)imidazo[4,5-*f*])-2,9-dimethyl-1,10-phenanthroline (*Neo*SH) and 4′-(2-mercaptopyridyl)-2,2′:6′,2″-terpyridine (*Ter*SH), both possessing the 2-mercaptopyridine (2-Mpy) group that will ensure the connection with the metallic surface and either a bidentate (*Neo*SH) or a tridentate (*Ter*SH) pendant group that will be used to generate the ruthenium complex. Both ligands have been used to stabilize and functionalize Au-NPs. The Au-NCs thus obtained have been used as effective platforms to functionalize Au-NPs by polypyridyl ruthenium complexes.

The design of the two heteroditopic ligands used in this article had to fulfil three main specifications: (i) the ligand had to efficiently complex the metallic centre on one side and (ii) strongly interact with the Au-NP surface on the other side. (iii) In order to facilitate potential electronic transfer between the ruthenium centre and the NP, a fully conjugated system was maintained between them. Concerning the specification (i), we decided to use either a tridentate terpyridine or a bidentate neocuproine (2,9-dimethyl-1,10-phenanthroline) to complex the metallic centre. Neocuproine was chosen instead of phenanthroline since the steric hindrance introduced by the two methyl groups prevents interaction of the nitrogen atoms with the Au-NP surface.[12] As to the specification (ii), we used the terminal 2-Mpy which provides two potential points of attachment to the Au-NP surface and therefore was expected to limit desorption processes. Interaction of 2-Mpy with Au-NPs and gold electrodes has already been studied.[13,14] The synthesis of both fully conjugated ligands was achieved using the 2-chloroisonicotinaldehyde (2-ClpyCHO). The aldehyde function can be used to generate different chelating pendant groups such as neocuproine and terpyridine, as shown in this communication, but other potentially interesting functional groups such as dipyrromethane or porphyrin might also be foreseen.[15] *Neo*SH and *Ter*SH were synthesized in two steps. In the first step, (4-(2-chloropyridyl)imidazo[4,5-*f*])-2,9-dimethyl-1,10-phenanthroline (*Neo*Cl) and 4′-(2-chloropyridyl)-2,2′:6′,2″-terpyridine (*Ter*Cl) were obtained by reaction of 2-ClpyCHO with 2,9-dimethyl-1,10-phenanthroline-5,6-dione (*Neo*dione) or 2-acetylpyridine, respectively. Both intermediates subsequently reacted with an excess of sodium hydrogensulfide to form *Neo*SH and *Ter*SH

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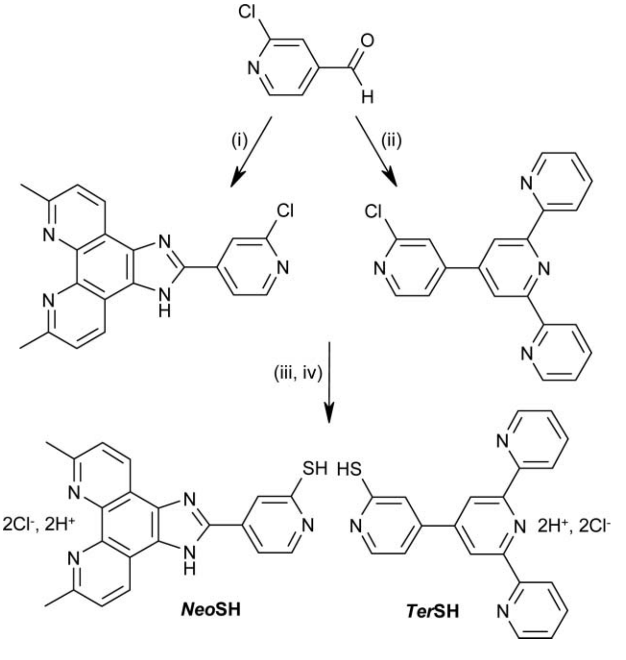
that were finally recovered as chloride salts of polypyridinium after precipitation with an excess of hydrochloric acid (Scheme 1). Detailed characterizations of *Neo*Cl, *Neo*SH, *Ter*Cl and *Ter*SH are given in the ESI.†

The syntheses of Au-NPs coated by *Neo*SH and *Ter*SH performed in DMF led to the best results in terms of stability and monodispersity in size of the final Au-NCs. Syntheses were also carried out in EtOH–H_2O (1 : 1) with *Ter*SH (*Neo*SH was poorly soluble in this mixed solvent) but polydisperse colloidal solutions were generally obtained, except when an excess of *Ter*SH was used (Fig. S3†). Stable colloidal solutions were obtained by addition of a DMF solution of $HAuCl_4$ to a mixture of *Ter*SH (or *Neo*SH) in DMF and reducing agent (aqueous solution of $NaBH_4$). In the remainder of this communication, we will mainly focus on the Au-NPs stabilized by *Ter*SH. The following results were obtained with an initial ratio $[Au^{3+}]/[TerSH] \approx 2.8$ but no noticeable alteration of the size distribution of the Au-NCs was observed for ratios between 2.5 and 3. Stable, reproducible and monodisperse Au-NPs with a diameter of 3.8 ± 0.6 nm were characterized in DMF, without formation of aggregates, as revealed by TEM (Fig. S4†). The as-synthesized Au-*Ter*SH-NCs were then efficiently purified. Addition of an excess of acetone to the DMF colloidal solution led to the flocculation of Au-*Ter*SH-NCs with the presence of few traces of free *Ter*SH. Free *Ter*SH was then removed either by successive re-solubilization in DMF and re-precipitation with an excess of acetone or by successive aqueous/non-aqueous solvent transfers using anionic exchanges around the NCs. As mentioned above, *Ter*SH was isolated as chloride salt of polypyridinium. Au-*Ter*SH-NCs are therefore positively charged and surrounded by easily exchangeable anions. The NCs can be dispersed in water, precipitated by addition of an excess of KPF_6, further re-dispersed in acetone (or in various organic solvents) as hexafluorophosphate salts, re-precipitated by addition of an excess of NBu_4Cl, re-dispersed in water as chloride salts and so forth. Using these successive solvent transfer processes, free ligands were efficiently removed while no noticeable change was detected in the size, shape and dispersity of the Au-NCs. The final precipitate can then be easily dispersed in a variety of solvents such as H_2O, EtOH, H_2O–EtOH (Fig. 1a), acetonitrile, DMF, DMSO. Concentration in Au-NPs up to 7×10^{-6} mol L^{-1} (1.2×10^{-2} mol L^{-1} in Au atoms) were obtained in water. A similar behaviour was observed using *Neo*SH except that smaller particles were obtained (diameter of 2.8 ± 0.5 nm) and the purification processes led to few aggregates in aqueous solution (Fig. S4).



Scheme 1 *Reagents and conditions*: (i) *Neo*dione, NH_4OAc, AcOH, 120 °C, 4 h, then NH_3; (ii) 2-acetylpyridine, KOH, MeOH, NH_3; (iii) NaSH, ethylene glycol, 140 °C, 12 h, then acetone; (iv) HCl.

The synthesis of Au-*Ter*SH-NCs and the purification processes were also studied by UV-vis spectroscopy (Fig. 1b). The spectrum of Au-*Ter*SH-NCs in DMF, before any purification, displays a surface plasmon resonance (SPR) at 536 nm, characteristic of the Au-NPs, and bands attributed to *Ter*SH. After purification using the solvent transfers and the anionic exchanges described above, the spectrum of Au-*Ter*SH-NCs dispersed in water exhibits a quasi-identical SPR confirming that the Au-NPs were not modified by the different treatments. The slight shift of the SPR from 536 to 531 nm was attributed to the modification of the solvent refractive index.[16] Another important feature of the UV-vis spectrum after purification concerns the disappearance of the two bands at 320 (shoulder) and 390 nm characteristic of the thione tautomer form of the mercaptopyridine group. 2-Mpy moieties are known to adsorb on Au-NPs in the thiol-like form while the thione tautomer form is expected for free 2-Mpy in solution.[14] Therefore, the disappearance of these two bands after purification can be used to confirm the efficiency of the removal of the non-grafted *Ter*SH ligands. UV-vis spectroscopy was also used to estimate the number of ligands per particle giving an average composition of $Au_{1667}TerSH_{90}$ (see ESI).

To illustrate the strength of the interaction of the 2-Mpy group with the gold surface, we compared the stabilization of Au-NPs with *Ter*SH and with (4′-pyridyl)-2,2′:6′,2″-terpyridine (*Ter*Py). The synthesis with *Ter*Py was realized in DMF following the procedure described above with *Ter*SH. After addition of the DMF solution of $HAuCl_4$ to the mixture of *Ter*Py and $NaBH_4$, the resulting solution turned blue and a precipitate was observed after few minutes. The pyridine pendant group ensured a much weaker interaction with the Au-NPs surface compared with the 2-Mpy pendant group. A stable colloidal DMF solution of Au-*Ter*Py-NCs was obtained only when a large excess of *Ter*Py was used to stabilize the Au-NPs.

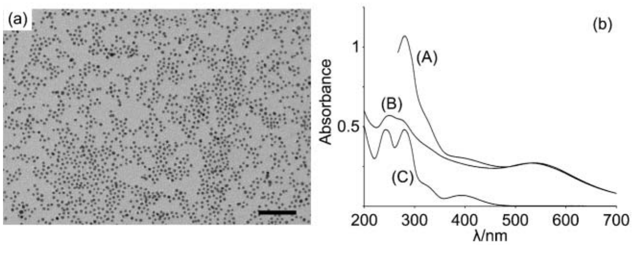


Fig. 1 (a) TEM image of Au-*Ter*SH-NCs synthesized in DMF, after purification and re-dispersion in H_2O–EtOH (v/v, 1 : 5). Scale: 50 nm. (b) Absorption spectra of Au-*Ter*SH-NCs in DMF before purification (A) and after purification and re-dispersion in H_2O–EtOH (B). Absorption spectrum of *Ter*SH in H_2O–EtOH (C).

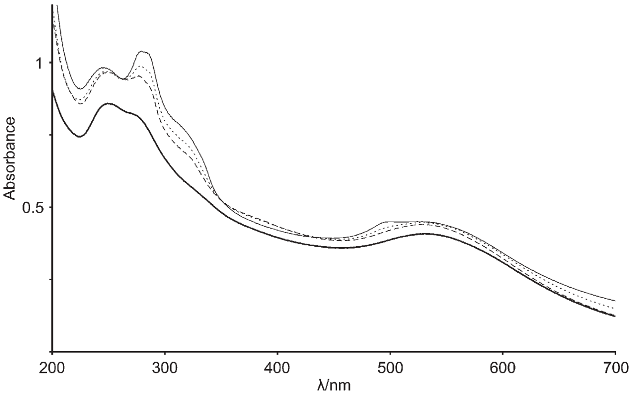


Fig. 2 Study of the reactivity of *Tolyl*TerpyRuCl$_3$ toward Au-*Ter*SH-NCs in H_2O–EtOH at 80 °C. Absorption spectra after 0 min (bold solid line), 80 min (dashed line), 240 min (dotted line) and 16 h (solid line).

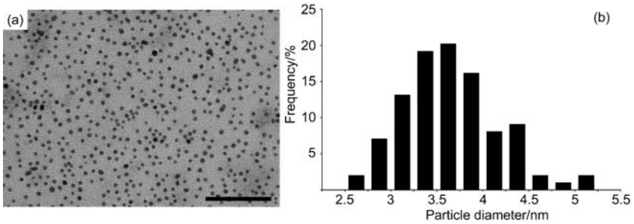


Fig. 3 (a) TEM image of the Au-[*tolyl*TerpyRu*Ter*SH]$^{2+}$-NCs obtained in H_2O–EtOH (v/v, 1 : 5). Scale: 50 nm. (b) Corresponding histogram.

The next step was to show that the monodisperse and purified Au-NCs characterized in this communication could be used as a platform for coordination chemistry. We studied the reactivity of *Tolyl*TerpyRuCl$_3$ (*Tolyl*Terpy: 4′-(4-tolyl)-2,2′:6′,2″-terpyridine) toward Au-*Ter*SH-NCs. The reaction was performed in a mixed solvent H_2O–EtOH (v/v, 1 : 5) at 80 °C and followed by UV-vis spectroscopy over a period of 16 h (Fig. 2). In order to understand this reactivity, we also studied independently the solubilization of *Tolyl*TerpyRuCl$_3$ and the reactivity of *Tolyl*TerpyRuCl$_3$ toward *Ter*Cl (instead of *Ter*SH to avoid the formation of disulfide complexes) using identical synthesis parameters (see ESI). These studies showed that the complexation of *Tolyl*TerpyRuCl$_3$ with Au-*Ter*SH-NCs proceeds in two steps. *Tolyl*TerpyRuCl$_3$ is first solubilized, as shown by the increase of the intensity of the band observed at *ca.* 385 nm, and then reacts with Au-*Ter*SH-NCs. The formation of the ruthenium complex [*Tolyl*TerpyRu*Ter*SH]$^{2+}$ is confirmed by the decrease of the band at *ca.* 385 nm and the concomitant increase of the bands at 280, 315 and 491 nm, characteristics of [*Tolyl*TerpyRu*Ter*SH]$^{2+}$ (Fig. 2). TEM analysis (Fig. 3) showed that the size, shape and dispersity of the Au-NCs were not noticeably affected by the reaction of complexation which further substantiates the high stability of the Au-*Ter*SH-NCs even when treated in refluxing H_2O–EtOH mixed solvent. Similar reactivity and stability were observed during the reaction of complexation of Au-*Neo*SH-NCs with (Phen)$_2$RuCl$_2$.

In conclusion, we have shown that the two heteroditopic ligands *Ter*SH and *Neo*SH could be used to efficiently stabilize and functionalize gold nanoparticles. The Au-*Ter*SH-NCs and Au-*Neo*SH-NCs presented in this communication showed an excellent monodispersity in size, can be easily purified and reversibly transferred from aqueous to organic medium without alteration of their size and shape. The strength of the interaction between the metallic surface and the 2-Mpy pendant group was exemplified by the grafting of ruthenium complexes with the Au-NCs in refluxing conditions. Monodisperse and solvent adaptable Au-NCs functionalized by fully conjugated ruthenium complexes have been obtained and their electrochemical, luminescence and NLO properties are currently investigated. This work is a breakthrough in facile coordination chemistry directly on pre-functionalized metallic nanoparticles. We currently use the terpyridine and neocuproine pendant group of the nanocomposites to generate fully conjugated (hetero)polymetallic complexes. Moreover the synthetic approach using the 2-chloroisonicotinaldehyde to obtain the heteroditopic ligands can be easily modified to generate a variety of potentially attractive pendant groups and therefore a large variety of metallic NPs functionalized by (poly)metallic complexes with tuneable physico-chemical properties.

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