Synthesis of wavelength-tunable luminescent gold and gold/silver nanodots†

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This paper describes the preparation of wavelength-tunable luminescent Au nanodots (NDs) and Au/Ag NDs at room temperature. Controlling the molar ratios of tetrakis(hydroxymethyl)phosphonium chloride (THPC) to Au ions and of Ag ions to Au ions allows the preparation of different sizes of Au and Au/Ag nanoparticles. We then used 11-mercaptoundecanoic acid (11-MUA) to react with the as-prepared nanoparticles to prepare wavelength-tunable luminescent 11-MUA–Au NDs and 11-MUA–Au/Ag NDs, respectively. Our prepared luminescent NDs exhibit a number of attractive optical properties: tunable luminescence wavelengths (456–640 nm), long lifetimes (>250 ns), and large Stokes shifts (>100 nm). These properties suggest that the as-prepared 11-MUA–Au NDs and 11-MUA–Au/Ag NDs would be suitable for use in sensing applications after bio-conjugation.

Introduction

Gold nanoparticles (Au NPs) exhibit size-dependent surface plasmon resonance (SPR) absorption properties when their conducting electrons in both the ground and excited states are confined to dimensions smaller than the electron mean free path (*ca.* 20 nm).[1–3] Unlike Au NPs having sizes greater than 4 nm, spherical gold nanodots (Au NDs) smaller than 2 nm that are protected by a monolayer of an alkanethiol or polymer exhibit luminescence properties as a consequence of quantum confinement effects.[4–12] Alkanethiol-bound Au NDs (RS–Au NDs) exhibit luminescence in the spectral region from the visible to the near-IR when excited in the UV region;[4–11] their emission quantum yields (QYs) are small (*ca.* 0.001–5%).[4–9] In contrast, Au NDs (diameter: <1 nm) protected by polyamidoamine (PAMAM) dendrimers or polyethylenimine (PEI) exhibit more stable and stronger (QY: >10%) luminescence properties relative to RS–Au NDs.[13,14]

Previously, we reported the preparation of RS–Au NDs of various sizes that fluoresced at wavelengths within the range 501–613 nm, with QYs ranging from 0.0062 to 3.1%.[15] We controlled the luminescence wavelength of these RS–Au NDs by varying the size of the alkanethiol. In this present investigation, we extended our study to the preparation of Au and Au/Ag NDs whose luminescence could be controlled by varying the molar ratios of tetrakis(hydroxymethyl)phosphonium chloride (THPC) to Au ions (for the Au NDs) and of Ag ions to Au ions (for the Au/Ag alloy NDs). First, we prepared a Au NP solution through reduction of $HAuCl_4 \cdot 3H_2O$ with THPC, which acted as both a reducing and capping agent.[16] Through variation of the initial mole ratio of THPC to hydrogen tetrachloroaurate(III) trihydrate ($HAuCl_4 \cdot 3H_2O$), we prepared Au NPs having diameters ranging from 2.2 to 3.7 nm. Introduction of 11-mercaptoundecanoic acid (11-MUA) ligands onto the surfaces of the as-prepared Au NPs resulted in luminescent 11-MUA–Au NDs. The as-prepared spherical 11-MUA–Au NDs of various sizes emitted light at different wavelengths within the range 500–640 nm. Likewise, by controlling the molar ratio of the Au and Ag ions, we prepared 11-MUA-protected Au/Ag NDs having similar sizes; these NDs emitted light at different wavelengths within the range 456–525 nm.

Materials and methods

Chemicals

Silver nitrate, 11-MUA, sodium borohydride, THPC and trisodium citrate dihydrate were purchased from Aldrich (Milwaukee, WI, USA). Sodium tetraborate and $HAuCl_4 \cdot 3H_2O$ were obtained from Acros (Geel, Belgium).

Preparation of THPC–Au NPs

The THPC–Au NPs were synthesized through reduction of $HAuCl_4 \cdot 3H_2O$ with THPC. A representative procedure is described: 1 M NaOH (1 mL; Aldrich) was diluted in water (50 mL) and then THPC solution (80% aqueous solution, 24 μL) was added. The resulting THPC solution (250 μL) was reacted for 5 min and then it was mixed with $HAuCl_4 \cdot 3H_2O$ solution (1.2 mM, 250 μL). The mixture was subjected to vortexing vigorously at ambient temperature and pressure for 15 min. The average size of the as-prepared THPC–Au NPs (3.4 ± 1.0 nm) was determined using a TEM (Tecnai 20 G2 S-Twin TEM, Philips/FEI, Hillsboro, Oregon).

Preparation of $NaBH_4$–Au NPs

The $NaBH_4$–Au NPs were synthesized through reduction of $HAuCl_4 \cdot 3H_2O$ with $NaBH_4$, according to a slight modification of a reported procedure.[17] An aqueous solution (20 mL) was

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prepared containing 0.25 mM $HAuCl_4$ and 0.25 mM trisodium citrate. Next, 0.01 M $NaBH_4$ solution (0.6 mL) was added in one portion into the $HAuCl_4$ solution under constant stirring. After stirring for another 30 s the solution turned brown, indicating the formation of the $NaBH_4$–Au NPs. The average size (3.3 ± 0.4 nm) of the as-prepared $NaBH_4$–Au NPs was determined using a TEM.

Preparation of luminescent 11-MUA–Au NDs

DI water (300 μL), trisodium tetraborate (50 mM, pH 9.2, 100 μL), 11-MUA (100 mM, 100 μL), and the as-prepared THPC– or $NaBH_4$–Au NPs (500 μL) were added sequentially to a 1.5 mL vial. The mixtures were then left to react for 72 h in the dark at room temperature to form the 11-MUA–Au NDs. We purified the fluorescent 11-MUA–Au NDs by conducting centrifugal filtration (13,500 g) for 40 min through a filter having a cutoff of 10 kDa. We then washed the pellets with 3.5 mL of tetraborate. Most of the 11-MUA and precursors in the solution were removed. We then measured the fluorescence of the removed solution, showing a very weak luminescence when excited at 375 nm. The results reveal that the luminescence signal is truly from 11-MUA–Au NDs. The absorption and luminescence spectra of the 11-MUA–Au NDs were recorded using a UV–Vis absorption spectrophotometer (Cintra 10e; GBC, Victoria, Australia) and a luminescence spectrophotometer (Cary Eclipse; Varian, CA, USA), respectively.

Preparation of luminescent 11-MUA–Au/Ag NDs

First, we prepared THPC–Au/Ag NPs in the presence of $AgNO_3$ at various Ag-to-Au ion molar ratios at a constant total ion concentration (0.6 mM) of Ag and Au; next, we subjected them to reactions with 11-MUA to prepare 11-MUA–Au/Ag NDs. Energy-dispersive X-ray spectroscopy (EDS) analysis of the 11-MUA–Au/Ag NDs using a 0.7 nm diameter electron probe was employed to determine their chemical identities. The measurements were conducted by illuminating an electron beam on a whole particle. The contents of Au^+ and Ag^+ ions were quantitatively determined by inductively coupled plasma mass spectrometry (ICP-MS) measurement.

Results and discussion

First, we prepared small Au NPs (sizes <4.0 nm) from $HAuCl_4$ by using two common reducing agents, THPC and $NaBH_4$, separately. When using $NaBH_4$, we added citrate (capping agent) to stabilize the as-prepared Au NPs. It is believed that THPC and $NaBH_4$ reduce Au^{3+} ions through the formation of formaldehyde and hydrogen, respectively.[16,17] Using transmission electron microscopy (TEM, Fig. 1), we determined (from counts of 100 particles) that the sizes of the spherical Au NPs formed through reduction of $HAuCl_4 \cdot 3H_2O$ with THPC and $NaBH_4$ were 3.4 (±1.0) and 3.3 (±0.4) nm, respectively. Herein, we denote the Au NPs prepared through reduction with THPC and $NaBH_4$ as THPC–Au NPs and $NaBH_4$–Au NPs, respectively. After reacting these NPs with 11-MUA (10 mM), which forms very strong covalent, distinctly directional Au–S bonds on the Au NP surfaces,[18,19] we obtained two sets of 11-MUA–Au NDs having sizes of 1.4 (±0.4) and 2.8 (±0.4) nm, respectively (Fig. 1). We believe that the sizes of these NDs decreased after treatment with 11-MUA because of producing significant fragmentation energies; *i.e.*, once the 11-MUA units adsorbed onto the Au NPs' surfaces, they tended to dissociate into smaller Au and Au–thiolate clusters.[18,19] The decrease in size from the THPC–Au NPs was greater than that from the $NaBH_4$–Au NPs, presumably because the citrate stabilization of the latter made it difficult for 11-MUA molecules to access the surface and etch the Au atoms. We suspect that the weak, but distinguishable, SPR absorption at 520 nm (curve D, Fig. 2a) of the solution is due to existence of some original $NaBH_4$–Au NPs. The solution does not exhibit luminescence (Fig. 2b). In contrast, the 11-MUA–Au NDs prepared from the THPC–Au NPs exhibited an absorption band centered at a wavelength (λ_{max}^{abs}) of 375 nm (extinction coefficient:

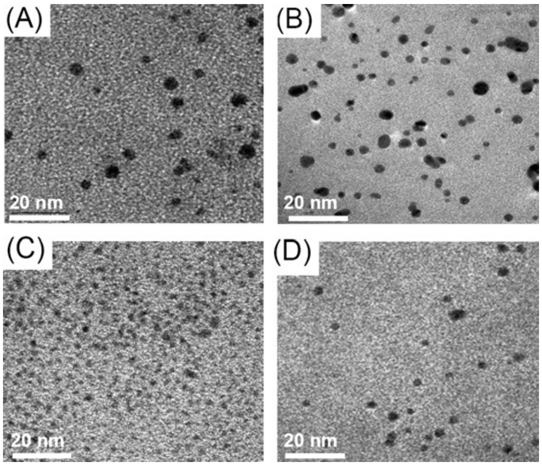

Fig. 1 TEM images of the (A) THPC–Au NPs, (B) $NaBH_4$–Au NPs, and (C, D) 11-MUA–Au NDs from (C) THPC–Au NPs and (D) $NaBH_4$–AuNPs after etching with 11-MUA.

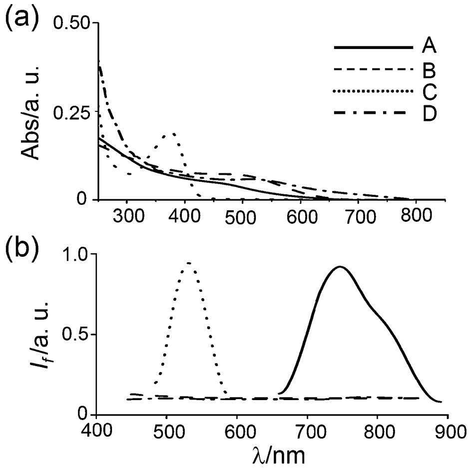

Fig. 2 (a) UV–Vis absorption spectra, (b) and normalized luminescence spectra of solutions of the (A) THPC–Au NPs, (B) $NaBH_4$–Au NPs, and (C, D) 11-MUA–Au NDs from (C) THPC–Au NPs and (D) $NaBH_4$–Au NPs after etching with 11-MUA. The normalized luminescence intensities (I_f) are plotted in arbitrary units (a. u.); excitation wavelength: 375 nm. In (b), the ratio of concentrations of solutions (A), (B), (C), and (D) was 23,000 : 23,000 : 1 : 23,000.

2.5×10^6 M^{-1} cm^{-1}) and stronger luminescence at 525 nm when excited at 375 nm (Fig. 2).

The absorption bands for 11-MUA–Au NDs are believed to originate from metal-centered (Au 5d^{10} to 6sp interband transitions) and/or ligand–metal charge transfer transitions.[4–11,20–22] The luminescence intensity at 525 nm of these NDs was *ca.* 23,000-fold higher than that of the THPC–Au NPs at 750 nm. Through comparison with quinine (QY = 53%), the QYs of the THPC–Au NPs and the 11-MUA–Au NDs prepared from them were 0.0001% and 4%, respectively. We demonstrate the purified 11-MUA–Au NDs sample was stable (no precipitates formed) for at least 3 months when stored at 4 °C in the dark by light scattering experiments. The intensities of static light scattering of fresh- and stored- 11-MUA–Au NDs (100 nM) were determined to be close (290 ± 15 kcps, n = 5) by using a particle size analyzer (Zetasizer Nano, Malvern). In addition, the luminescence intensity of the stored 11-MUA–Au NDs was almost the same as that of the freshly prepared ones (Fig. S1†). The as-prepared 11-MUA–Au NDs from THPC–Au NPs had a Stokes shift of 150 nm and lifetimes (t_1/t_2) of 274/1134 ns by fitting to a biexponential luminescence decay (Fig. 3). Large Stokes-shifted luminescence with long lifetimes is a general characteristic of thiol–Au(I) complexes that display ligand–metal charge transfer and metal(I)–metal(I) interactions.[20–22] Thus, we suspect that our brightly luminescent 11-MUA–Au NDs were Au ND/polynuclear Au(I)–thiol (core/shell) complexes.

We obtained differently sized THPC–Au NPs upon varying the THPC-to-$HAuCl_4$ molar ratio, which controlled the seeding and growth rates. First, we prepared THPC–Au NPs by varying this molar ratio over the range 1.0–3.5; then we subjected the as-prepared THPC–Au NPs to reactions with 11-MUA to form 11-MUA–Au NDs. Fig. 4 reveals that this strategy resulted in differently sized 11-MUA–Au NDs that emitted colors ranging from green to reddish (Fig. S2†), with corresponding emission wavelengths ranging from 500 to 640 nm. The corresponding TEM images (Fig. S3†) indicated that the THPC–Au NPs prepared from $HAuCl_4$ (0.6 mM) at THPC-to-$HAuCl_4$ molar ratios of 1.0, 2.0, and 3.5 were well dispersed and had average diameters of 3.6 (±2.1), 2.9 (±0.6), and 2.2 (±0.6) nm, respectively. Thus, upon increasing the THPC-to-$HAuCl_4$ molar ratio, the sizes of the THPC–Au NPs decreased, primarily because of the higher seeding rate in the presence of a larger amount of reducing agent.[17] Fig. 4 presents the luminescence spectra of the three 11-MUA–Au ND solutions that we prepared from the three differently sized THPC–Au NPs. Because these three 11-MUA–Au ND solutions possessed different luminescence QYs, their luminescence spectra are presented after normalization.

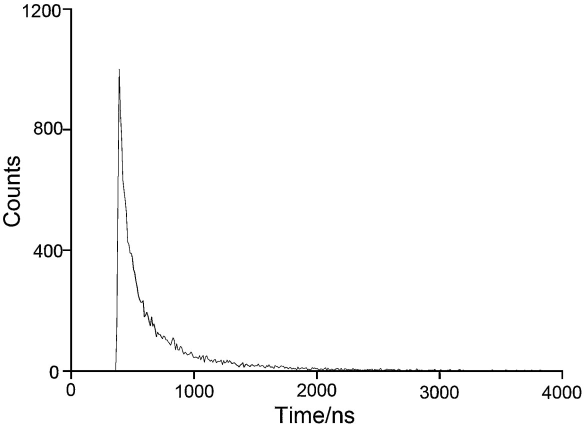

Fig. 3 Luminescence lifetime, after excitation at 375 nm, of the 11-MUA–Au NDs prepared from the THPC–Au NPs. The luminescence decay was fitted to a biexponential decay. Other conditions were the same as those described in Fig. 2.

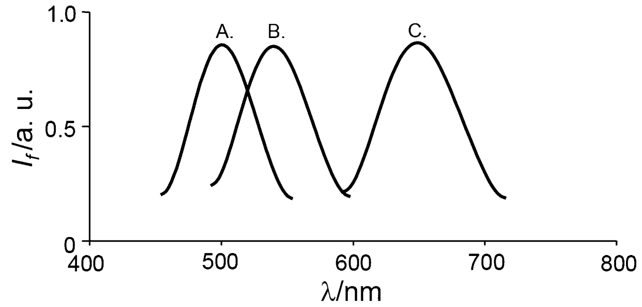

Fig. 4 Normalized luminescence spectra of 11-MUA–Au NDs prepared at THPC-to-$HAuCl_4$ concentration ratios of (A) 1.0, (B) 2.0, and (C) 3.5. Excitation wavelengths: (A) 400, (B) 370, and (C) 276 nm. The concentration ratio of solutions (A), (B), and (C) was 1.5 : 1.0 : 151.8.

Table 1 provides a comparison of the sizes and optical properties of the three as-prepared 11-MUA–Au NDs. The size distribution histograms of 11-MUA–Au NDs are displayed in Fig. S4 (see ESI†). It is interesting that we obtained smaller 11-MUA–Au NDs from the larger-sized THPC–Au NPs. We suspect that because the smaller THPC–Au NPs were prepared at greater THPC-to-$HAuCl_4$ molar ratios, the excess of THPC in solution inhibited the 11-MUA molecules from accessing the surface and etching the Au NPs. The larger 11-MUA–Au NDs exhibited emissions at longer wavelengths; *e.g.*, the 1.2 (±0.2)- and 2.1 (±0.1)-nm 11-MUA–Au NDs emitted light at 500 and 640 nm, respectively. Presumably the luminescence wavelength underwent a blue shift upon decreasing the THPC-to-$HAuCl_4$ molar ratio primarily because of the decreased ND size (Table 1) and increased the contribution of the 11-MUA–passivated surfaces, which decreased the energy gap between the quantized levels as a result of a smaller core and a higher coverage of thiolate.[20] Our reasoning was supported by the facts of long life times and a large Stokes shift of the 11-MUA–Au NDs. Like quantum dots, the fluorescence of 11-MUA–Au NDs is dependent on many parameters, including the nature and size of the NDs, the surface, and solution composition.

To probe the detailed electronic structure of the 11-MUA–Au NDs, we used X-ray photoelectron spectroscopy (XPS) to

Table 1 Sizes and optical properties of 11-MUA–Au NDs prepared at various ratios of [THPC]-to-[$HAuCl_4$] ratios

[THPC]/[$HAuCl_4$]	Size (nm)	λ_{max}^{ex} (nm)	λ_{max}^{em} (nm)	QY	Binding energy (eV) of Au($4f_{7/2}$)
1.0	1.2 ± 0.2	400	500	3.8%	84.90
2.0	1.7 ± 0.2	370	550	3.9%	84.25
3.5	2.1 ± 0.1	276	640	0.2%	84.05

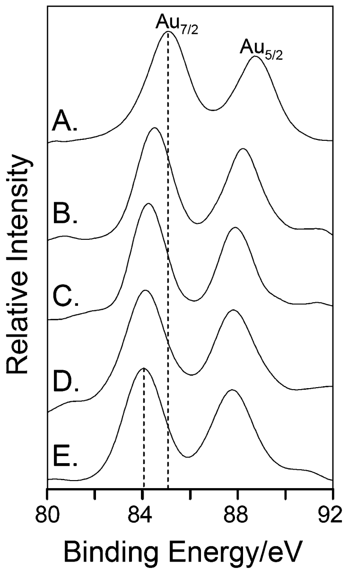

Fig. 5 Au 4f core-level photoelectron spectra of (A) the Au(I) complex, (B–D) the 11-MUA–Au NDs of various sizes, and (E) a Au evaporated film dosed onto silicon substrates and measured at room temperature. The mean diameters of the NDs were (B) 1.2, (C) 1.7, and (D) 2.1 nm.

investigate the oxidation states of their surfaces (Fig. 5). Table 1 lists the binding energies (BE) of the Au $4f_{7/2}$ electrons, a common signature for Au oxidation states when using the BE (285.3 eV) of the alkyl chain C 1s orbital as an internal reference.[23] The BEs for the Au $4f_{7/2}$ electrons in the 11-MUA–Au NDs fell within the region from 84.02 eV (Au) to 85.00 eV (polynuclear Au(I)–11-MUA complex). The smaller 11-MUA–Au NDs exhibited greater shifts to higher BE for their Au $4f_{7/2}$ electrons, relative to that of bulk Au crystallites. Upon decreasing the particle diameter, the NDs have a higher ratio of 11-MUA-bonded surface Au atoms relative to atoms in the bulk. The BE shifted to a greater extent for the smaller NDs because of the greater contribution of the 11-MUA–passivated surfaces (*i.e.*, the higher-BE component) to the Au_{4f} core-level photoemission spectrum.[24]

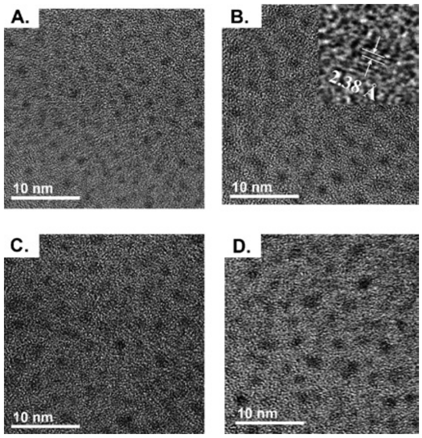

Fig. 6 TEM images of the 11-MUA–Au/Ag NDs prepared at Ag-to-Au ratios of (A) 0, (B) 0.125, (C) 0.800, and (D) 2.000. Inset to (B) is the high-resolution TEM image. Other conditions were the same as those described in Fig. 2.

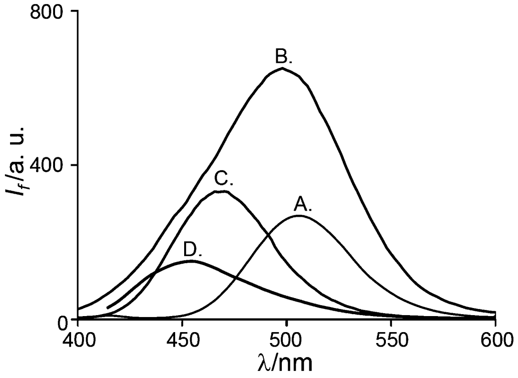

Fig. 7 Luminescence spectra of 11-MUA–Au/Ag NDs prepared at $AgNO_3$-to-$HAuCl_4$ molar ratios of (A) 0, (B) 0.125, (C) 0.800, and (D) 2.000, respectively. Excitation wavelengths: (A) 375 nm; (B)–(D) 330 nm.

We then investigated the effect of $AgNO_3$ on the preparation of luminescent Au/Ag NDs. We suspected that these NPs and NDs were both Au/Ag alloys because there we observed no obvious lattice mismatch or core/shell-like structure (Fig. 6).[25,26] The observed lattice constant (2.38 Å) corresponds to the *d*-spacing of the (111) crystal plane of an fcc structure. It has been reported that Au/Ag NPs have lattice constants that resemble those of Ag and Au NPs.[25,26] The EDS spectrum of the 11-MUA–Au/Ag NDs prepared at an Ag-to-Au molar ratio of 2.0 is shown in Fig. S5 (see ESI†), indicating the presence of Ag and Au in the NDs and also C, O, and S from the 11-MUA molecules. The Cu peaks are due to the copper grid used in the sample preparation. The ratio of Ag/Au was determined from AgL and AuL lines to be 1.52, which agrees with that (1.60) obtained by ICP-MS measurements. Fig. 7 indicates that the as-prepared 11-MUA–Au/Ag NDs had tunable luminescence properties at wavelengths ranging from 456 to 525 nm. From analyses of TEM images, we estimated that the THPC–Au/Ag NPs and 11-MUA–Au/Ag NDs had sizes of 2.6 (±0.7) and 1.7 (±0.3) nm, respectively (Fig. 6). The size distribution histograms of 11-MUA–Au/Ag NDs are displayed in Fig. S6 (see ESI†). Upon increasing the concentration of $AgNO_3$, the emitted colors of the 11-MUA–Au/Ag NDs range from yellow to blue (Fig. S7†), with corresponding emission wavelengths ranging from 525 to 456 nm. It has been suggested that deposition of Ag atoms onto Au NPs causes a blue shift in the SPR absorption.[27] Thus, we suspected that the luminescence properties of these 11-MUA–Au/Ag NDs were related to their Au/Ag molar ratios. We confirmed this suspicion by conducting ICP-MS measurements (Table 2). The ICP-MS data reveal that the Ag contents in the 11-MUA–Au/Ag NDs were higher when the NDs were prepared in solutions containing higher concentrations of $AgNO_3$.

To further investigate the blue-shift of these 11-MUA–Au/Ag NDs upon increasing the Ag content, we prepared a series of mixtures of 11-MUA (10 mM), $HAuCl_4$, and $AgNO_3$, with Ag^+-to-Au^{3+} molar ratios of 0, 0.20, 0.50, 0.67, 1.00, and 1.50 at a constant total ion concentration (0.3 mM) of Au^{3+} and Ag^+. Upon increasing the Ag^+ concentration, the luminescence at 620 nm decreased, but that at 445 nm increased (Fig. S8†); note that luminescence at 445 nm is a characteristic of $Ag(SR)_n$ clusters.[28]

Table 2 Sizes, optical properties, and Ag-to-Au mole ratios of 11-MUA–Au/Ag NDs prepared at various [$AgNO_3$]-to-[$HAuCl_4$] ratios

[$AgNO_3$]/[$HAuCl_4$]	Size (nm)	λ_{max}^{ex} (nm)	λ_{max}^{em} (nm)	QY	Ag/Au[a]
0	1.4 ± 0.2	375	525	1.9%	0
0.125	1.7 ± 0.1	330	500	3.2%	0.12
0.800	1.6 ± 0.2	330	478	2.3%	0.64
2.000	1.7 ± 0.2	330	456	0.5%	1.60

[a] Calculated from the ICP-MS data.

It has been reported that organic-soluble tiopronin-coated Ag clusters (1.6 nm) react with Au(I)[$SCH_2(C_6H_4)C(CH_3)_3$] to form Ag/Au bimetallic cores, with a concomitant red-shift of the luminescence.[29] The behavior of our 11-MUA–Au/Ag NDs is consistent with those findings; *i.e.*, the blue shift in the as-prepared 11-MUA–Au/Ag NDs was due primarily to an increased Ag content.

Conclusions

We have demonstrated that controlling the THPC-to-$HAuCl_4$ molar ratio allows tuning of the luminescence wavelength of 11-MUA–Au NDs. We have also demonstrated the preparation of 11-MUA–Au/Ag NDs that emit luminescence at tunable wavelengths within the region from 456 to 525 nm. Our prepared 11-MUA–Au NDs and 11-MUA–Au/Ag NDs exhibit a number of attractive optical properties: tunable luminescence wavelengths, long lifetimes (>250 ns), and large Stokes shifts (>100 nm). These properties suggest that the as-prepared 11-MUA–Au NDs and 11-MUA–Au/Ag NDs would be suitable for use in sensing applications after bio-conjugation.[30–34] Much like semiconductor quantum dots (QDs), the highly size- and surface-dependent luminescence properties of these NDs are also very sensitive to the environment.[34–36] Unlike semiconductor QDs, however, the QYs of luminescent Au NDs are lower. Nevertheless, these luminescent NDs are easy to prepare, exhibit good batch-to-batch reproducibility (relative standard deviation: <5% from 10 batches) in terms of their luminescence intensity, and have low toxicity.[37–40] Although the QYs of our thus-prepared luminescent Au NDs are lower than those of dendrimer-protected Au clusters (*ca.* Au_{40}),[20] the 11-MUA–Au NDs (*ca.* Au_{250}) and 11-MUA–Au/Ag NDs are readily purified and/or separated from the other matrix components through simple centrifugal filtration (membrane cutoff: 10 kDa). Indeed, we have successfully applied functionalized fluorescent Au NDs for sensing proteins in biological samples and mercury ion in environmental samples.[15,40]

Acknowledgements

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