

Strongly Luminescent Films Fabricated by Thermolysis of Gold–Thiolate Complexes in a Polymer Matrix

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We present a simple method for the fabrication of highly luminescent gold-containing films by thermal decomposition of gold(I) dodecylthiolate synthesized by treating an ethanol solution of gold tetrachloroauric acid with an ethanol solution of 1-dodecanethiol. During the heat treatment of gold(I) dodecylthiolate complexes homogeneously distributed in the polystyrene matrix, extinction spectra of the films change from the well resolved spectrum of a gold(I) thiolate complex peaked at 390 nm to the broad plasmon peak of metallic gold centered around 600 nm. All samples, both before and after heat treatment, show a strong red emission, with a maximum in the spectral range of 620–640 nm. The room temperature emission quantum yield strongly increases from the nonheated films to the briefly heated films reaching a value of ~8%, and decreases for the samples where larger gold particles are formed after prolonged heating. Transmission electron microscopy shows the occurrence of monodisperse gold nanoparticles with 1.8 nm mean diameter in the polymer matrix. Extended heat treatment leads to the partial coalescence of these nanoparticles into larger particles of irregular shapes, with a size in the range of 10–200 nm. We explain these findings by the formation from the original luminescent Au(I)–thiolate complexes of an emissive species with even stronger luminescence. This species is consumed in the growth of larger Au particles upon further heating. From the spectroscopic data, the strongly luminescent species could be few-atom thiolated Au clusters or polynuclear Au(I)–thiolate complexes with strong aurophilic interactions.

Introduction

A large variety of novel functional materials can be obtained by incorporating metal nanoparticles into polymer matrices. Embedding magnetic metal nanoparticles into polymer films provides transparent layers suitable for magneto-optical applications.¹ Polarizers, dichroic devices, ultrahigh refractive index materials can be produced by combining polymers with different types of nanosized metal particles.^{2,3} Significant body of literature is devoted to the formation of noble metal nanoparticles in polymer matrices.^{4–6} Selvan et al. reported on the formation of subnanometer sized gold particles with a polypyrrole shell in a block copolymer matrix.⁴ Rogach et al. showed generation of silver nanopar-

ticles and nanowires in a polyvinylalcohol matrix under UV illumination.⁵ Corbierre and co-workers described the synthesis of gold nanoparticles decorated with covalently bound thiolcapped polystyrene macromolecules incorporated in a polystyrene matrix.⁶ The Murray group used monolayer-protected nanoparticles to prepare single noble metal and alloy films.⁷

Recently, photoluminescence (PL) has been observed from extremely small gold nanoparticles (often denoted as clusters) prepared by reduction of metal salts in the presence of

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specific capping ligands.^{8–23} There are several books²⁴ and review articles^{25,26} summarizing the synthetic methods that lead to the formation of gold nanoparticles/clusters and discussing their luminescence mechanisms.^{27,28} The PL quantum yield (QY) of gold clusters strongly depends on the specific method of synthesis since it is determined to a large extent by the nature of ligands, as will be specifically addressed in our discussion below. It varies by up to 5 orders of magnitude. One of the first observations of visible luminescence (QY 1×10^{-4} to 1×10^{-5}) from gold nanoclusters ascribed to the interband sp-d transition was reported by Wilcoxon et al.⁸ Bigioni et al. reported on the near-infrared luminescence of gold nanoparticles of sizes of 1.1 and 1.7 nm, with energy gaps of 0.9 eV for the former and 0.5 eV for the latter and the QY of $\sim 0.005\%$.⁹ Huang et al. reported a broad emission centered around 770 nm for their 1.8 nm gold particles, with a PL QY of up to 0.3%.¹⁰ Investigating the optical properties of what was believed to be Au₂₈ clusters (whose core composition has been very recently shown to be Au₂₅)^{29,30} Link et al. found two emission maxima around 1.5 and 1.15 eV, and explained their findings within the solid state and the molecular model.^{11,12} In the former, the lower energy luminescence originates from intraband transitions in the sp band, whereas the higher energy photons are due to interband transitions between the d and sp bands. In the latter, the molecular model, fluorescence is the source of the higher energy luminescence while a phosphorescence transition is responsible for the lower energy emission.

Negishi et al. introduced a very reasonable terminology for gold nanospecies of different sizes,¹³ in which thiolated gold clusters with a closed shell structure of a well defined “magic” size (often denoted as “monolayer-protected clusters” or even “cluster molecules”)²⁶ bridge the gap between gold(I)–thiolate complexes and thiolate-protected gold nanocrystals. The Au_n clusters ($n = 10–39$) reported in refs.^{13,21} showed size-dependent optical properties and a PL QY between 1×10^{-6} and 1×10^{-3} . Duan et al. synthesized green- and blue-emitting luminescent Au₈ gold clusters by etching of 8 nm gold nanoparticles, which show much higher QY (10–20%) than previously reported clusters.¹⁴ Even larger PL QY of 41% has been reported for Au₈ clusters encapsulated within poly(amidoamine) (PAMAM) dendrim-

ers by Zheng et al.¹⁵ The dominant (93%) short lifetime component of 7.5 ns of the blue emission observed was ascribed to singlet interband transitions between the d- and sp-bands, and another, long lifetime component to a triplet-singlet intraband transition. The use of a dendrimer cage-like capping, which effectively protects the Au clusters from quenchers present in the solution, was claimed as the reason for the dramatically enhanced PL QY. One year later, the same group tuned the emission of differently sized gold clusters from the UV to the near-infrared, reporting QYs between 10% for NIR to 70% for UV.¹⁶ An observation of strong blue photoluminescence from OH-terminated PAMAM dendrimers in the absence of gold clusters^{31,32} contradicted the results of refs.^{15,16} and was addressed by Zheng et al. in ref.²⁸ with a series of experiments underpinning their previous results. No emission has been reported, to the best of our knowledge, for the widely studied Au₅₅(PPh₃)₁₂Cl₆ clusters^{27,33} (PPh₃ being triphenylphosphine).

We note that the thiolate complexes of gold(I), which are very often used as precursors of Au clusters and nanocrystals, are also light-emitting species, whose emission characteristics may resemble those of gold clusters. The photoluminescence properties of gold(I) complexes, with phenylphosphines and thioates as the most common ligands have been addressed in a plenty of publications^{34–40} and summarized in several books^{24,41} and review articles.⁴² Emission of Au(I) complexes has been considered to be a characteristic property of compounds displaying weak Au(I)–Au(I) bonds (the effect often referred to as “aurophilicity”), which are attributed to the stabilization of filled 5d metal orbitals by the interaction with empty 6s/6p-based molecular orbitals, coming close in energy because of the strong relativistic effect possessed by gold.⁴³ The strength of Au(I)–Au(I) bonding interactions in different complexes influences their luminescence transitions resulting in variations of the emission energies (typically in the visible spectral range, and very often in the red^{35,37,38,40}). The emission pathways discussed in particular for Au(I)–thiolate complexes in ref. 34 are a ligand-to-metal charge transfer (LMCT) from the sulfur group of the thiolate ligand to one of the gold atoms and subsequent radiative relaxation of that Au atom, but also other mechanisms like ligand-to-(metal–metal bond) charge transfer (LMMCT) transitions taking into account aurophilic

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interactions of Au(I) have been suggested.⁴⁴ The emission of Au(I) complexes has been commonly observed in the solid state^{36,37,39} where the Au–Au distances are smaller than 3.6 Å, but has been also reported for solutions-based compounds.^{35,36} Typical PL lifetimes measured for luminescent Au(I) complexes were in the range of 2–8 μs^{34,35,40} evidencing on the phosphorescent nature of the emission processes, and QYs reported were up to 0.14% in solutions at room temperature.³⁵

In this paper, we present a method of fabrication of strongly luminescent gold-containing films that makes use of a thermal decomposition of gold thiolates in molten polymer phase.^{45,46} This very simple approach is especially suitable for the large-scale production of luminescent plastics based on molecular gold additives, because the gold thiolates can be added to thermoplastic polymers during the processing stage. Gold nanoparticles are generated inside the polystyrene matrix by thermal decomposition of gold(I) dodecylthiolate synthesized by treating an ethanol solution of gold tetrachloroauric acid with an ethanol solution of 1-dodecanethiol. We provide data on the optical and structural characteristics of the samples and discuss the origin of their strong red PL based on the literature reviewed above.

Experimental Section

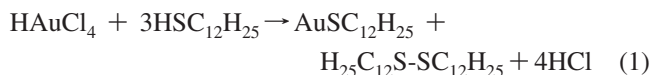
UV–vis extinction and excitation spectra were recorded with a Cary 50 spectrophotometer (Varian). Time-integrated fluorescence spectra were recorded at room temperature with a Cary Eclipse spectrofluorimeter (Varian). The room-temperature PL QY of Au-containing films was estimated by comparison with Rhodamine 6G (laser grade, Lambda Physik) in ethanol solution (Uvasol). The angle of incidence for the PL QY measurements was 30°, detection was at 90° relative to illumination, and excitation was at 350 nm.

Time-resolved fluorescence spectroscopy was performed on a Picoquant Fluotime 200 spectrometer. The samples were excited with pulsed laser light ($\lambda_{\text{ex}} = 405$ nm) from a Picoquant LDH–P–C–405 pulsed diode laser at an angle of incidence of 60°. Repetition rates of 2 MHz (cw power of 7.8 μW) and 10 MHz (cw power of 18 μW) were used. The fluorescence was collected at 90°. Scattered excitation light was blocked with a Schott GG 435 glass filter. The fluorescence light was spectrally resolved with a Science-Tech 9030 monochromator set to $\lambda_{\text{em}} = 670$ nm (slit widths: 8 nm) and detected with a fast photomultiplier tube. Fluorescence photons were counted with a Picoquant Timeharp 200 TCSPC board for 300 s. The obtained fluorescence decay curves were corrected for dark counts and the impulse response and normalized to their peak values. The time resolution for the measurements was 1.2 ns.

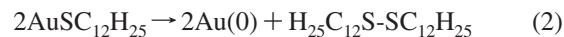
X-ray diffraction (XRD) spectra were taken on a Rigaku DMAX–IIIC diffractometer. Transmission electron microscopy (TEM) images were recorded on a JEOL JEM-1011 electron microscope at an accelerating voltage of 100 kV. Samples for TEM were prepared by dissolution of the gold-containing polymer matrix in toluene, placing a drop of the resulting solutions on carbon-coated TEM copper grids and wiping them off with a filter paper after 30 s. Thermo-gravimetric analysis and differential scanning calorimetry have been carried out with TA-Instruments model Q.500 and model Q.100 systems, respectively.

Results and Discussion

Following the method of ref 46 gold(I) dodecylthiolate (Au-DDT, AuSC₁₂H₂₅) has been used as a precursor to generate gold clusters and gold nanoparticles in the polystyrene (PS) matrix. This compound was synthesized at room temperature under vigorous stirring by a dropwise addition of an ethanol solution of 1-dodecanethiol (C₁₂H₂₅SH) to an ethanol solution of gold tetrachloroauric acid (HAuCl₄·3H₂O) according to the following reaction



In the preparation of gold dodecylthiolate, gold salt and thiol were used in stoichiometric amount (1:3) according to reaction 1. Two moles of thiol were required for the reduction of one mole of Au(III) to Au(I), with disulfide as a byproduct, and one additional mole of thiol was required to precipitate the obtained Au(I) as thiolate (AuSC₁₂H₂₅), as confirmed by thermogravimetric analysis. The yellow precipitate was separated by filtration, washed with acetone, and finely dispersed in a chloroform solution of amorphous PS (M_w 230 000 g mol⁻¹) under intensive sonication for a few minutes. The solution was cast on a planar glass surface and allowed to dry resulting in an optically transparent thin (0.1–0.3 mm) solid PS/AuSC₁₂H₂₅ film containing ca. 10 wt % AuSC₁₂H₂₅. The thermal treatment required to decompose the gold dodecylthiolate was done by placing a thin film of PS/Au thiolate blend between an aluminum foil and a flat glass cover and applying heating with a hot plate at a constant temperature of 300 °C maintained by a heat controller for 40 s, 60 and 105 s, respectively. The resulting film samples, denoted by *Au-40s*, *Au-60s*, and *Au-105s* hereafter, have been used for further studies, together with a nonheated sample of a solid PS/AuSC₁₂H₂₅ blend, which we denote by *Au-DDT*. Upon heating, the reduction of AuSC₁₂H₂₅ to Au(0) takes place as a result of Au(I) thiolate thermolysis, with a formation of disulfide as a side product



Thermogravimetric analysis of the gold(I) dodecylthiolate showed a single weight loss at ca. 300 °C, caused by evaporation of organic byproduct originating from disulfide molecules. The experimentally determined residual weight (49.5%) corresponds exactly to the theoretical value for a pure gold phase formation.

Optical properties of the gold-containing polymer films have been studied by UV–vis extinction and excitation spectroscopy as well as by time-integrated and time-resolved PL spectroscopy. Extinction spectra of the samples are shown in Figure 1. For all samples, the extinction below 275 nm is dominated by the extinction of the PS matrix. The nonheated *Au-DDT* sample shows two pronounced characteristic absorption peaks at 360 and 390 nm, which are also present in the solution of gold(I) dodecylthiolate (not shown). They are not present in the extinction spectrum of the *Au-40s* sample, indicating that within 40 s of heat treatment AuSC₁₂H₂₅ has been completely decomposed and transformed to some other species. A characteristic gold plasmon absorption band

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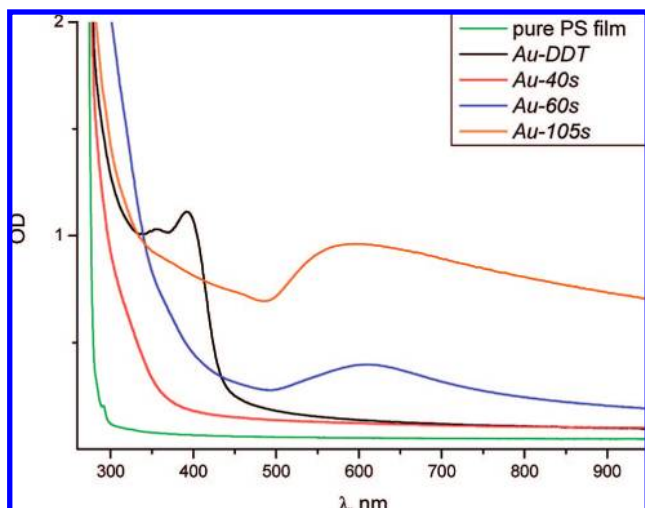


Figure 1. Extinction spectra of the gold-containing film samples, as indicated in the frame.

appears at around 600 nm for the *Au-60s* sample and grows in strength for the *Au-105s* sample, which contains larger gold particles. Neither the *Au-DDT* sample nor the *Au-40s* sample shows significant plasmon absorption.

Remarkably, all gold-containing film samples, as well as the solution of gold(I) dodecylthiolate in toluene emit red light under UV excitation (Figure 2). Figure 3 shows emission spectra of the samples, with a single peak located between 550 and 750 nm. The emission maxima are at 623 nm for the *Au-DDT* and the *Au-40s* samples, 633 nm for the *Au-60s* sample and 640 nm for the *Au-105s* sample. The *Au-DDT* complex in solution shows a very similar emission band with a maximum at 620 nm. The PS matrix itself exhibits some luminescence near 750 nm. The PL QY of the film samples at room temperature was estimated by comparison with Rhodamin 6G in ethanol solution. The resulting numbers (Table 1) should be considered as rough estimates due to the inherent difficulty of measuring the QY of strongly absorbing and strongly scattering films. The tendency in changing the PL QY, however, is clear: it increases by more than an order of magnitude from the nonheated *Au-DDT* to the *Au-40s* sample, reaching an impressive value of approximately 8%, decreases by a factor of ~ 2 for *Au-60s*, and drops strongly upon further heating for *Au-105s*. Figure 3 also shows PL excitation (PLE) spectra of the samples, where the detection wavelength is kept at 680 nm and the excitation wavelength is scanned. In all samples, PL is the strongest when exciting between 275 and 350 nm and very weak for excitation between 450 and 550 nm. *Au-40s* is the only sample that can efficiently be excited below 275 nm. We also note that there is a large Stokes shift between the excitation and emission energies for all the luminescent samples (Figure 3, Table 1), which points on the phosphorescence nature of their emission similar to the previously reported gold(I)–alkanethiolate complexes.^{36,38}

Time-resolved PL decays of the samples at emission wavelengths between 570 and 800 nm were measured with a pulsed laser diode operating at 405 nm. At this excitation wavelength, the absorption of all samples is relatively weak. The PL dynamics is similar in all samples: the luminescence

decays are nonexponential; a fast decay (nanosecond range) is followed by a slower decay in the μs range. The lifetimes resulting from a three-exponential fit of the decays are summarized in Table 1. The fast and slow decay components are clearly distinct, but the fit of the slow decay with two exponentials does not necessarily reflect the underlying physics; a continuous distribution of lifetimes in the μs range is more adequate. The amplitude of the nanosecond range decay decreases steadily from 570 to 800 nm. In contrast, the amplitude of the slow decay components peaks near the maximum emission wavelengths observed in the time-integrated PL measurements. The slow decay dominates the overall luminescence in the wavelength range between 570 and 800 nm: the fraction of photons emitted in the slow decay is 90% for *Au-DDT*, 97% for *Au-40s*, and 96% for *Au-60s*. For the weakly luminescent *Au-105s*, it still amounts to 80%. This is in contrast to the results of ref 15 on light-emitting dendrimer-capped Au nanoclusters where microsecond and nanosecond range decay components were also observed but the contribution of the slow component was only 7%. The long PL lifetime (microsecond) of the dominant component of our samples may be an indication of its surface-state-related origin, determined by the Au–S interactions with thiolate molecules.

TEM micrographs taken on the film samples show presence of spherical monodisperse gold nanoparticles, 1.8 nm in diameter, for both the nonheated *Au-DDT* sample (Figure 4a) and for the *Au-40s* sample (Figure 4b). In the nonheated sample, they could have been formed either in polymer matrix or even in solution due to the photoassisted reduction^{47,48} of gold(I) thiolate being analogous to the heat-assisted thermolysis (reaction 2). According to their size, these particles can be considered as being on the border between thiolated gold clusters and thiolate-protected gold nanocrystals.^{13,26} The core size of a gold nanocluster consisting of 145 atoms has been estimated as 1.7 nm in ref 9 while the cluster composition of Au_{201} has been ascribed to the samples with core diameter of 1.8 nm in ref 17. The particles observed are typically not sintered or agglomerated together but separated by a thin dielectric phase (polymer and/or thiolate shell). If the formation of monodisperse 1.8 nm Au particles preferentially takes place upon heat-assisted thermolysis according to reaction 2, the high viscosity of the PS matrix may play an essential role. In particular, the spontaneous formation of monodisperse particles is related to the high particle nucleation rate caused by the high heating temperature, which leads to the rapid thermal decomposition of the $\text{AuSC}_{12}\text{H}_{25}$ precursor and thus to the formation of a large amount of gold atoms. Under the high supersaturation level, which is maintained during the initial stages of the heating process, gold particle nuclei are continuously generated by clustering of Au atoms, but their coalescence and growth are prohibited or sufficiently slowed down by the limited diffusion in a viscous polymer matrix. Consequently, monodisperse gold particles homogeneously distributed within the PS matrix are obtained upon heating, due to reduction of $\text{AuSC}_{12}\text{H}_{25}$ to Au(0) as a result of Au(I) thiolate

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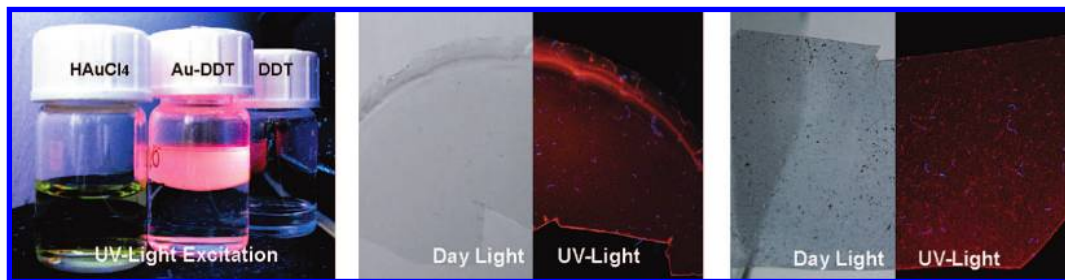


Figure 2. Photographs showing the red emission from the samples of gold(I) dodecylthiolate in toluene (left), the *Au-40s* film sample (middle), and the *Au-60s* film sample (right).

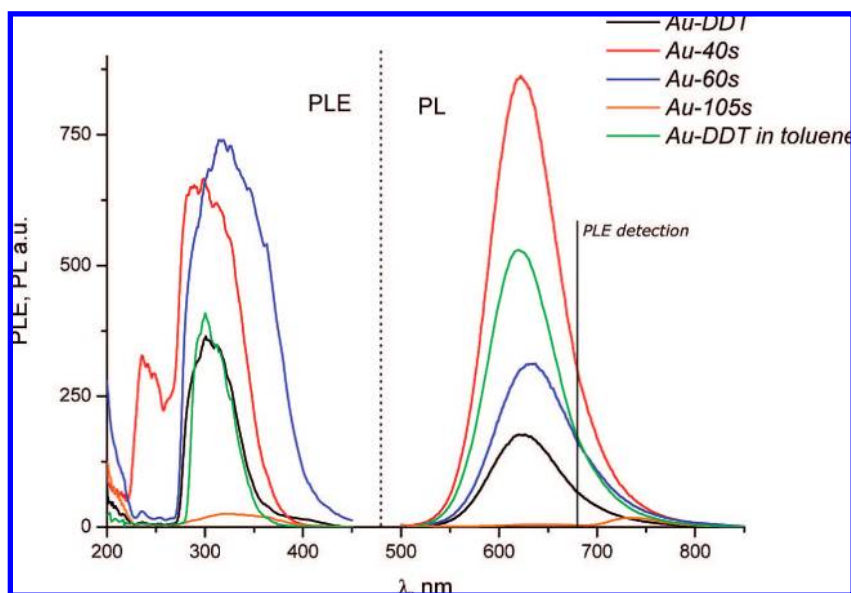


Figure 3. PL excitation (left) and PL (right) spectra of the luminescent gold-containing films and the Au-DDT complex in toluene solution (see figure legend for details). For the PLE spectra, the detection wavelength was set at 680 nm for all measurements; the angle of incidence for the PL measurements on films was 30°, detection was at 60° relative to illumination. For the PL spectra, the excitation was at the respective optimal wavelength (see text); the angle of incidence for the PL measurements on films was 30°, detection was at 90° relative to illumination.

Table 1. Luminescence Properties of Gold-Containing Films

sample	<i>Au-DDT</i>	<i>Au-40s</i>	<i>Au-60s</i>	<i>Au-105s</i>
emission energy (eV)	1.99	1.99	1.96	1.94
excitation energy (eV)	>2.81	>3.1	>2.58	>3.1
Stokes shift (eV)	>0.82	>1.11	>0.62	>1.16
PL QY (%)	0.6	8	3	0.2
luminescence lifetimes (μ s)	1.25/0.22/0.02	1.75/0.25/0.01	1.85/0.34/0.03	1.18/0.15/0.01

thermolysis (reaction 2), with volatile disulfides⁷ starting to form because of decomposition of thiolates at 300 °C as has been proved by thermogravimetric analysis. The surface of 1.8 nm gold particles may still remain protected by the remaining thiolate molecules, in addition to their space confinement within the PS matrix.

TEM images of the *Au-60s* and *Au-105s* samples reveal that further heat treatment results in the partial coalescence of 1.8 nm gold particles into much larger gold particles of irregular shapes, with a size in the range of 10–200 nm (images c and d in Figure 4). As the viscous polymer matrix slows down the diffusion of nanoparticles, a significant amount of the 1.8 nm particles can still be found in TEM images of both *Au-60s* and *Au-105s* samples. X-ray powder diffraction spectra of the polystyrene/Au-DDT blend (20% by weight of Au-DDT, in order to increase the XRD signal) reveal the formation of a crystalline face-centered cubic (fcc)

gold phase. The value of the lattice constant calculated from the XRD pattern is 3.991 ± 0.002 Å, which is very close to the value for bulk fcc gold phase.

Comparing the optical properties of our gold-containing samples with literature data on luminescent Au clusters and Au(I)–thiolate complexes, the following conclusions can be made. Most studies on thiolated monolayer-protected gold clusters report emission in the near-infrared,^{8,10,17–19} whereas our samples show red luminescence at 620–640 nm. The PL QYs estimated for our samples are considerably larger than typical PL QYs reported for gold clusters in the literature,^{9,11,13,18} with the notable exception of the Au₁₁ cluster of ref. 19 capped by triphenylphosphine and DDT, as well as dendrimer-capped few-atom clusters of ref 16, whose emission was shown to be tuneable through the visible spectral range and further into the near-infrared (although not between 600 and 700 nm). It appears that for Au clusters

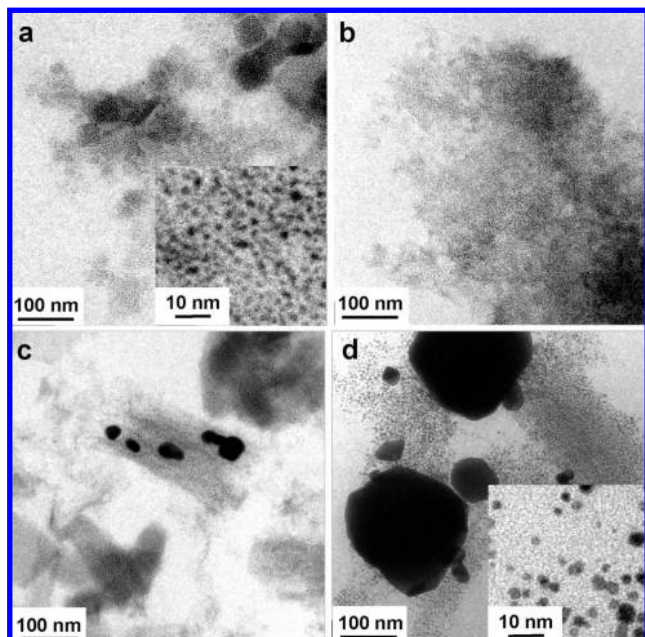
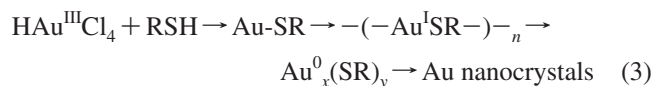


Figure 4. TEM images of the gold-containing film samples: (a) *Au-DDT*, (b) *Au-40s*, (c) *Au-60s*, and (d) *Au-105s*. Insets in (a) and (d) show regions with nanoparticles that are typically observed in the respective samples at higher magnification.

confined in dendrimers^{15,16,28} (amide ligands) the emission wavelengths are sensitive to their size (or, better to say, to the number of atoms in a few-atom cluster), while for the thiolated Au clusters the emission is typically observed in the near-infrared and is much less sensitive to the cluster size. The nature of ligands on few-atom Au clusters plays a vital role in determination of their emission properties so far. This was directly confirmed for Au₁₁ cluster which did not exhibit any luminescence being originally protected with a shell of triphenylphosphine and showed emission in near-infrared upon surface exchange reaction with DDT.¹⁸ In ref 10 the emission wavelength of 1.4–1.9 nm gold particles was found to vary specifically with the protecting sulfur-containing ligands.

The dendrimer-capped Au clusters emit on a very different time scale, with dominant lifetimes not exceeding 10 ns,¹⁵ whereas our samples show dominant emission in the μ s time range. Both the excitation and the emission spectra of our samples resemble the spectra of Au₁₂ clusters protected by dimercaptosuccinic acid.²¹ The authors of ref 21 notice, however, that although their few-atom gold clusters are categorized into the family of gold monolayer-protected clusters, their properties are similar in many aspects to gold(I)–thiolate complexes. Indeed, the emission and excitation spectra of our samples strongly resemble those of Au(I) thiolate complexes reported in refs 34, 35, 37, and 38 with similar PL decay times.

For the samples produced at the conditions of our experiment, the reduction of Au(III) by thiols (RSH) to an Au(I)–SR, followed by thermal decomposition of the polynuclear Au(I)–thiolate complexes $-(\text{Au}^{\text{I}}\text{SR})_n-$ to thiolated Au_x(SR)_y clusters (also called monolayer-protected cluster molecules²⁶) and further to thiolate-protected gold nanocrystals takes place, which can be illustrated by the following reaction scheme



It is difficult to define a clear border between the polynuclear Au(I)–thiolate complexes $-(\text{Au}^{\text{I}}\text{SR})_n-$ with strong aurophilic interactions and the thiolated Au_x(SR)_y clusters consisting of only a few Au atoms coordinated with thiol molecules, with both Au–Au and Au–SR bonds being present in both cases. Au(I)–thiolate complexes are often polynuclear,²⁴ with reported stoichiometries including e.g. Au₁₀(SR)₁₀ and Au₁₂(SR)₁₂. They consist of two interpenetrating gold–gold pentagon (for Au₁₀) or hexagon (for Au₁₂) rings, both structures being stabilized by “aurophilic” Au(I)–Au(I) interactions.⁴⁹

In this light, we interpret the heat-induced changes in the structural and optical properties of our luminescent gold-containing polymer films as follows. The Au(I) dodecylthiolate complex, which is an emissive species similar to the Au(I)–thiolate luminescent complexes of refs 34, 38, and 40 is transformed to other emissive species during the first 40 s of heating. This is evidenced by the disappearance of its extinction peak at 360 nm. These emissive species may be few-atom gold thiolated clusters, such as the Au₁₂ clusters of ref 21, which show more than 10 times stronger luminescence (located at a similar wavelength) than the initially luminescent Au(I) dodecylthiolate complexes (Table 1). It is also possible that the reduction is incomplete yielding partially rearranged Au(I)-based complexes with an altered degree of polymerization, which affects the degree of aurophilic Au(I)–Au(I) interactions and thus gives rise to an increased photoluminescence.^{37,44} Further investigations will be focused on elucidating the nature of the emissive species in our samples and on revealing the mechanism of their emission.

The monodisperse gold nanoparticles of 1.8 nm size observed in the TEM images of all our samples (including nonheated *Au-DDT* films, where they can form by photo-assisted reduction of gold(I) thiolate complexes) consist of several hundreds of Au atoms (like Au₁₄₅ in ref 9 or Au₂₀₁ in ref 17), and it is very unlikely that they can emit light with a significant QY in the visible spectral range.^{9,10,19} Upon further heating, a broad plasmon absorption peak of metallic gold centered around 600 nm appears and the PL QY of the samples decreases, which indicates the formation of larger gold nanocrystals (clearly observed in TEM) at the expense of both luminescent gold cluster or complexes and 1.8 nm gold particles.

Conclusions

In conclusion, we have presented a simple technique for the fabrication of gold-containing polymer films by thermal decomposition of gold(I) dodecylthiolate, which strongly emit at 620–640 nm. During heat treatment, the extinction spectra of such films change from the well-resolved spectrum of a gold(I) thiolate complex, which peaks at 390 nm, to the broad plasmon peak of metallic gold centered around 600

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nm. Transmission electron microscopy shows the formation of monodisperse gold nanoparticles with 1.8 nm mean diameter well-separated by the polymer. Prolonged heat treatment for more than 40 s leads to the partial coalescence of the initially formed 1.8 nm gold nanoparticles into larger particles of irregular shapes, with sizes in the range of 10–200 nm. We ascribe the PL properties of our samples to the formation from the original luminescent Au(I)–thiolate complexes of an emissive species with even stronger luminescence. This species is consumed in the growth of larger Au particles, which starts between 40 and 60 s of heating. From the spectroscopic data, the strongly luminescent species could be few-atom thiolated Au clusters or rearranged Au(I)-based complexes with an altered degree of polymerization, which affects the degree of aurophilic Au(I)–Au(I) interactions and thus gives rise to an increased photoluminescence. Further studies are required to elucidate the precise nature of the emissive species in our samples, which we have tentatively identified as Au(I)–thiolate complexes or few-atoms thiolated $\text{Au}^0_x(\text{SR})_y$ clusters. We note that from the spectroscopic data few-atom thiolated Au clusters are difficult to distinguish from polynuclear Au(I)–thiolate complexes with strong aurophilic interactions.

Polymer films incorporating gold nanoparticles of different sizes are potentially interesting for decorative applications.^{24,45} The luminescent polymer samples reported here, with their exceptionally stable (over months) emission may find applications in optoelectronics, in particular in nanoparticle-based LEDs.⁵⁰ Both light-emitting Au(I)–thiolate complexes or few-atom thiolated $\text{Au}^0_x(\text{SR})_y$ clusters may find application as nontoxic fluorescent labels in cell imaging^{51–53} and sensing^{54,55} applications.

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