

Versatile Synthesis of Functional Gold Nanoparticles: Grafting Polymers From and Onto

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Functionalized gold nanoparticles have been prepared in an organic solvent by a two-phase reduction method in ethyl acetate and water using bis(6-hydroxyhexyl) disulfide bis(2-bromoisobutyl) ester, bis(6-acetyloxyhexyl) disulfide, and bis(5-carboxypentyl) disulfide bis(pentafluorophenyl) ester as stabilizing ligands. This procedure features the advantages that no phase transfer agent was necessary during the preparation of the gold nanoparticles and that the reducing conditions were mild enough to utilize functional disulfide ligands. The obtained gold nanoparticles with typical sizes between 2 and 5 nm could be precipitated and redispersed without any irreversible aggregation. Using these nanoparticles the stimuli-responsive polymers poly(*N*-isopropylacrylamide) and poly(*N*-cyclopropylacrylamide) could be grafted from the surface. Also, the grafting of polymers onto gold nanoparticles could be demonstrated with nanoparticles featuring pentafluorophenyl ester groups. The reactive character of gold nanoparticles featuring a pentafluorophenyl ester groups on the surface could also be applied in the preparation of multilayers on the basis of covalent bonds between the gold nanoparticles and polyallylamine.

Introduction

Interest in gold nanoparticles (AuNP) has risen exponentially in the past two decades, and several literature reviews^{1–4} can be consulted, documenting the importance of this area of nanochemistry. The unique optical properties of gold nanoparticles, the versatility of their synthesis, and the possibility to functionalize them in a wide variety of ways has led to various applications and research interests such as the deposition of gold nanoparticles on planar surfaces,^{5,6} measurements of a distance-dependent energy transfer from a nearby chromophore,^{7–9} catalytic activity in the preparation of polysiloxanes,¹⁰ siloxane nanowires, tubes, and fibers;¹¹ and sensors for the detection of biological species^{12–15} or

for small molecules¹⁶ or detecting DNA sequences by an anisotropic functionalization of gold nanoparticles,¹⁷ to mention a few. A multipurpose strategy can be found in the composition of a hybrid consisting of gold nanoparticles and a polymeric material as this enables the development of novel materials, which possess both the gold optical properties and the manifold opportunities modern polymer chemistry has to offer.

The standard way to synthesize gold nanoparticles is the reduction of a gold(III) compound in the presence of a stabilizing ligand, such as a thiol, disulfide, or amine. Many protocols using various solvents, ligands, and reducing agents and sometimes further additives have been presented. Very common is the reduction of auric acid in water using citrate, which also serves as stabilizing ligand.¹⁸ The resulting particles have usually diameters in the range of 13–15 nm.^{6,12,19–21} The exchange of citrate by thiols has been described,^{21–25} whereas difficulty of this ligand exchange has also been mentioned.²⁶

A popular method working in an organic solvent is the procedure by Schiffrin and Brust.^{27–29} In their method, tetrachloroauric acid is transferred into toluene by help of an excess of tetraoctylammonium bromide. Alkylthiols,

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ω -hydroxyalkylthiols,³⁰ or other functionalized ligands¹⁰ have been employed during the reduction with sodium tetraborohydride in water. Ligands on the gold surface may also be exchanged afterward.^{13,16,31,32} A synthetic route to gold nanoparticles in an organic solvent without the use of a transfer agent was published by Yee et al.³³ They dissolved tetrachloroauric acid in dry THF, a thiol or another ligand (e.g., polymer prepared by RAFT process^{34,35}) was added, and the reduction with lithium triethylborohydride yielded AuNPs. Also, amines have been reported to act as both reducing and stabilizing agent in the synthesis of gold nanoparticles.^{26,36–38} Aniline³⁹ and pyrrole⁴⁰ can be oxidized by auric acid to result in polymers and gold nanoparticles. Other one-phase syntheses of gold nanoparticles in methanol⁴¹ or ethanol⁴² using a slow addition of sodium tetraborohydride have been published.

There are two principal pathways that lead to composites of a nanoparticle and a polymeric material. In a grafting-to approach, an aforesynthesized polymeric ligand is attached to the surface. This ligand can be present during the reduction step,^{43–45} or it can substitute another ligand, which was used during the particle formation step.^{21,23} A surface-initiated polymerization,^{31,32,41,42,46} on the other hand, is a grafting-from technique and usually results in a higher ligand density

on the surface because the surface may be densely covered with small initiator molecules and, theoretically, each of these can grow a polymer chain. In a grafting-to method, however, macromolecules approach the surface as a coiled chain and therefore take up more space than a stretched chain would.^{47–49}

Within this communication we describe a new synthesis of ester-functionalized gold nanoparticles that facilitates a two-phase approach and therefore very mild reduction conditions without the requirement of a phase transfer agent. Using this technique, we explored the possibility to attach a variety of functional ligands to gold nanoparticle surfaces. Surface-initiated controlled radical polymerization led to stimulus responsive materials with optical properties of the gold cores and the thermoresponsive behavior of the polymeric shell. The reduction step in the synthesis was mild enough to allow the surface functionalization of gold nanoparticles with active esters. These functional groups could be used to chemically bind gold nanoparticles to amino-functionalized surfaces as well as graft amino end-functionalized polymers onto AuNPs, thereby widening the chemical functionality of gold nanoparticles.

Experimental Section

Materials. All chemicals were purchased from Acros, Aldrich, or Fluka. Pentafluorophenol (99%) was obtained from Alfa Aesar. All reagents were used as received unless stated otherwise. CuBr was extracted several times with glacial acetic acid under reflux, washed with methanol, and dried in vacuum. *N*-Isopropylacrylamide was recrystallized from toluene/hexane. Tetrahydrofuran was distilled from sodium. Methyl methacrylate was distilled from calcium hydride under reduced pressure. Dichloromethane was distilled from phosphor pentoxide.

Instrumentation. All ¹H NMR spectra were recorded on a Bruker 300 MHz FT-NMR spectrometer. Chemical shifts (δ) were given in ppm relative to TMS. Size exclusion chromatography (SEC) was used to determine molecular weights and molecular weight distributions, M_w/M_n , of polymer samples with respect to polystyrene standards (PSS). Thermogravimetric analysis was performed using a Perkin-Elmer Pyris 6 TGA under a nitrogen atmosphere.

Bis(6-hydroxyhexyl) Disulfide (1). 1.34 g of iodine (5.30 mmol) was dissolved in 34 mL of diethyl ether, 1.2 mL of 1-mercapto-6-hexanol (8.82 mmol) was added, and the mixture was stirred at room temperature. After 30 min, 353 mg of NaOH (8.82 mmol) dissolved in 15 mL of water was added, and stirring was continued overnight. After another addition of 80 mg of NaOH (2 mmol) in 5 mL of water, 20 mL of extra diethyl ether was added, and the mixture was extracted with an aqueous solution of sodium sulfite until the organic layer was colorless. The aqueous layer was washed with a little amount of diethyl ether, the organic phases were combined and dried with magnesium sulfate, and the solvent was removed. Quantitative yield. ¹H NMR (CDCl₃): δ = 3.62 (t, J = 6.5 Hz, 4H, HOCH₂), 2.66 (t, J = 7.4 Hz, 4H, SCH₂), 1.72–1.61 (m, 4H, HOCH₂CH₂), 1.60–1.50 (m, 4H, SCH₂CH₂), 1.38–1.3 (m, 8H, CH₂CH₂).

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Bis(6-hydroxyhexyl) Disulfide Bis(2-bromoisobutyl) Ester (2). To 4.41 mmol of bis(6-hydroxyhexyl) disulfide dissolved in 20 mL of dry diethyl ether and cooled to 0 °C was added 1 mL of dry pyridine (12.3 mmol). Under stirring, 1.4 mL of 2-bromoisobutyl bromide (11.32 mmol) was added slowly in a nitrogen atmosphere. The reaction was allowed to warm to room temperature overnight. Water was added carefully, and the mixture was extracted with diluted hydrochloric acid, water, diluted aqueous NaOH solution, and water again. The organic phase was dried (magnesium sulfate), and removal of the solvent yielded 2.02 g (82%) of raw product which could be purified by column chromatography (ethyl acetate/hexane 1:1) to give 1.85 g (74%) of pure product. ¹H NMR (CDCl₃): δ = 4.08 (t, *J* = 6.5 Hz, 4H, COOCH₂), 2.59 (t, *J* = 7.2 Hz, 4H, SCH₂), 1.84 (s, 12H, CH₃), 1.65–1.56 (m, 8H, COOCH₂CH₂, SCH₂CH₂), 1.40–1.28 (m, 8H, CH₂CH₂). ¹³C NMR (CDCl₃): δ = 171.6 (COO), 65.9 (CH₂O), 55.9 (CBr), 38.8 (CH₂S), 30.8 (CH₃), 29.0 (CH₂CH₂S), 28.2 (CH₂CH₂O), 28.0 (CH₂CH₂CH₂S), 25.4 (CH₂CH₂CH₂O). FT-IR (ν/cm⁻¹): 2928, 2856 (C–H), 1731 (C=O), 1462, 1273, 1159, 1107.

Bis(6-acetyloxyhexyl) Disulfide (3). 1.65 g of bis(6-hydroxyhexyl) disulfide (6.2 mmol), 1.83 mL of triethylamine (13.0 mmol), and 14 mL of dry dichloromethane were combined in a round-bottom flask equipped with a magnetic stir bar. The flask was flushed with argon, closed with a septum, and immersed into an ice bath. Slowly, 1.07 g of acetyl chloride (13.6 mmol) was injected with constant stirring. The reaction was allowed to warm to room temperature overnight, the precipitated salt was removed by suction filtration, and the filtrate was extracted with water several times. The organic phase was dried with magnesium sulfate and the solvent removed. 1.65 g (76%) of pure product was obtained. ¹H NMR (CDCl₃): δ = 4.01 (t, *J* = 6.6 Hz, 4H, OCH₂), 2.63 (t, *J* = 7.2 Hz, 4H, SCH₂), 2.00 (s, 6H, CH₃), 1.70–1.55 (m, 8H, OCH₂CH₂, CH₂CH₂S), 1.44–1.27 (m, 8H, CH₂CH₂). ¹³C NMR (CDCl₃): δ = 171.1 (COO), 64.4 (CH₂O), 38.8 (CH₂S), 29.0 (CH₂CH₂S), 28.4 (CH₂CH₂O), 28.0 (CH₂CH₂CH₂S), 25.5 (CH₂CH₂CH₂O), 20.9 (CH₃). FT-IR (ν/cm⁻¹): 2930, 2857 (C–H), 1734 (C=O), 1364, 1232, 1122 (w), 1045.

Bis(5-carboxypentyl) Disulfide (4). In analogy to a literature procedure,⁵⁰ 15.79 g of 6-bromohexanoic acid (81 mmol) was dissolved in 50 mL of water and 50 mL of methanol containing 7.5 g of sodium hydrogen carbonate (89 mmol). After gas evolution had stopped, 30.53 g of sodium thiosulfate (123 mmol) was added, and the mixture was heated to reflux for 6 h. The solvent was removed to yield a white crystalline substance, which was not further characterized. It was dissolved in 500 mL of 10% hydrochloric acid, and 6.44 g of thiourea (85 mmol) was added. All components readily dissolved as the mixture was stirred. After 2 weeks of stirring at room temperature the product had precipitated. Product can also be collected after a shorter period by filtration, but the mother liquor should be kept, as product will continue to precipitate. Heating shortened the reaction time to a few hours but also increased the amount of side products. 10.4 g (87%) of bis(5-carboxypentyl) disulfide could thus be collected. ¹H NMR (CDCl₃): δ = 2.66 (t, *J* = 7.2 Hz, 4H, CH₂COOH), 2.35 (t, *J* = 7.4 Hz, 4H, SCH₂), 1.73–1.59 (m, 8H, SCH₂CH₂, CH₂CH₂COOH), 1.48–1.38 (m, 4H, CH₂CH₂CH₂).

Bis(5-chlorocarbonylpentyl) Disulfide. 1.3 g of bis(5-carboxypentyl) disulfide (4) (4.42 mmol), 22 mL of dry hexane, and 1 mL of thionyl chloride were mixed and heated to reflux. The acid dissolved upon heating. After 3 h the mixture was cooled and two phases separated. Hexane and excess thionyl chloride were removed by distillation under reduced pressure. 1.28 g (88%) of product

was obtained which was not purified any further. ¹H NMR (CDCl₃): δ = 2.88 (t, *J* = 7.2 Hz, 4H, COCH₂), 2.64 (t, *J* = 7.2 Hz, 4H, SCH₂), 1.76–1.63 (m, 8H, COCH₂CH₂, CH₂CH₂S), 1.51–1.38 (m, 4H, CH₂CH₂CH₂).

Bis(5-carboxypentyl) Disulfide Bis(pentafluorophenyl) Ester (5). A mixture of 2.63 g of pentafluorophenol (7.13 mmol) and 1.74 mL of 2,6-lutidine (7.49 mmol) in 8 mL of dry dichloromethane was cooled to 0 °C, and 2.6 g of bis(5-chlorocarbonylpentyl) disulfide (7.85 mmol) dissolved in 3 mL of dry dichloromethane was added dropwise through a septum. The reaction was stirred overnight while it was allowed to warm to room temperature. The mixture was extracted with water several times, and the organic phase was dried (magnesium sulfate) and the solvent removed. The crude product was purified by column chromatography with chloroform as the eluent. 3.37 g (76%) of product was obtained. ¹H NMR (CDCl₃): δ = 2.71–2.64 (app quart, *J* = 7.0 Hz, 8H, COCH₂, SCH₂), 1.85–1.68 (m, 8H, COCH₂CH₂, SCH₂CH₂), 1.56–1.46 (m, 4H, CH₂CH₂CH₂). ¹³C NMR (CDCl₃): δ = 169.3 (COO), 142.8, 141.1, 139.6, 137.7, 136.2 (arom), 38.5 (CH₂S), 33.1 (CH₂CO), 28.6 (CH₂CH₂S), 27.6 (CH₂CH₂CH₂CO), 24.3 (CH₂CH₂CO). ¹⁹F NMR (CDCl₃): δ = –153.2 (d, 2F, *J* = 7.5 Hz), –158.5 (t, 1F, *J* = 21 Hz), –162.8 (t, 2F, *J* = 21 Hz). FT-IR (ν/cm⁻¹): 2936, 2862 (C–H), 1788 (C=O), 1467 (w), 1093, 991 (arom), 757 (w).

Cyclopropyl Acrylamide. A solution of 7 mL of cyclopropylamine (101.2 mmol) and 15.6 mL of triethylamine (111.3 mmol) in 100 mL of chloroform was cooled to 0 °C in a nitrogen atmosphere, and 9.97 mL of acryloyl chloride (121 mmol) was added dropwise. The reaction was allowed to warm to room temperature overnight and extracted several times with water. The raw product still contained triethylamine and acrylic acid (NMR) and was therefore first recrystallized from diethyl ether and then distilled under reduced pressure. At 80 °C and 5 × 10⁻² mbar, 2.7 g (24%) of a colorless liquid was obtained which crystallized upon cooling. ¹H NMR (CDCl₃): δ = 6.22 (d, *J* = 7.4 Hz, 1H, CH₂=CH), 6.06 (dd, *J* = 3.4 and 5.7 Hz, CHH=CH), 5.57 (d, *J* = 6.1 Hz, 1H, CHH=CH), 2.75 (m, 1H, NHCH), 0.74 (m, 2H, CH₂), 0.51 (m, 2H, CH₂).

Synthesis of Gold Nanoparticles. In a typical experiment, 153 mg of tetrachloroauric acid trihydrate (388 μmol) was dissolved in 40 mL of ethyl acetate (p.a.). After addition of 175 μmol of disulfide (Au:S ratio of 1:0.9), the mixture was stirred for 10 min at room temperature to guarantee that the ligand was dissolved homogeneously. Then, a freshly prepared solution of 150 mg of sodium borohydride (3.9 mmol) in 3.5 mL of water was injected very rapidly under vigorous stirring. After 15 s the organic layer was washed intensively with water several times and dried with magnesium sulfate, which was filtered off and washed with ethyl acetate. The dispersion was concentrated to about 15 mL by distilling of the solvent at reduced pressure and a maximum temperature of 30 °C. Complete drying of the dispersion was also possible and did not affect the redispersibility of the nanoparticles.

To purify the colloids from excess ligand, a concentrated dispersion was poured into a 10–20-fold excess of hexane and centrifuged at 4000 rpm for 5 min. The colorless hexane was decanted (and evaporated to recover the excess ligand), and the sedimented gold nanoparticles were dissolved in 3 mL of tetrahydrofuran and again precipitated and centrifuged from hexane. This procedure was repeated until no disulfide could be detected in the discarded hexane anymore. After the last washing step, the gold nanoparticles were redispersed in the solvent required for a following reaction (e.g., distilled THF) and stored at –20 °C.

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Surface-Initiated Polymerization of *N*-Isopropylacrylamide/*N*-Cyclopropylacrylamide (PNiPaam@AuNP/PCyPaam@AuNP). A typical procedure was as follows. Gold nanoparticles produced from 153 mg of tetrachloroauric acid dissolved in distilled tetrahydrofuran and a magnetic stir bar were placed in a Schlenck flask. While immersed in a room temperature water bath the solvent was removed from the flask by applying vacuum. Stirring prevented the mixture from sputtering excessively. After complete evaporation of the solvent the flask was refilled with argon and kept until the following steps were carried out. A second Schlenck flask was filled with 1.1 g of recrystallized *N*-isopropylacrylamide (9.73 mmol), 2 mL of freshly distilled tetrahydrofuran, 2 mL of Milli-Q grade water, and 9.5 mg of copper(I) bromide (66.25 μ mol). This second flask was degassed once by freeze–pump–thawing and refilled with argon. 27.6 μ L of *N,N,N',N'',N'''*-pentamethyldiethylenetriamine (PMDETA) (132.5 μ mol) was added under an argon atmosphere, and the resulting mixture was again degassed by three freeze–pump–thaw cycles. After refilling with argon for the last time the content of the second flask was transferred into the first flask containing the dried initiator coated gold nanoparticles via an argon-flushed cannula. Complete redispersion of gold nanoparticles was assured by cautiously shaking the flask. Then, the polymerization mixture was stirred at room temperature for 45 h.

Polymerization of *N*-cyclopropylacrylamide followed exactly the same steps: All reagents apart from the monomer were used similarly. The employed amounts were gold nanoparticles from 106 mg of tetrachloroauric acid trihydrate (269 μ mol), 617 mg of *N*-cyclopropylacrylamide (5.56 mmol), 11.5 μ L of PMDETA (55.2 μ mol), 8 mg of CuBr (55.8 μ mol), and 2 mL of THF/water 1:1.

In order to isolate the polymeric product, the solvents were completely removed by applying vacuum to the reaction while the Schlenck flask was kept at room temperature. The dried contents were dissolved in THF and poured into an excess of diethyl ether. The precipitated colored material was separated by centrifugation and the colorless diethyl ether discarded. The polymeric product was then dried in vacuum.

Polymerization of PNiPaam yielded 190 mg (14% monomer conversion) of hybrid material; 70 mg (8% monomer conversion) of PCyPaam on gold was obtained.

Surface-Initiated Polymerization of Methyl Methacrylate (PMMA@AuNP). The same protocol as for *N*-isopropylacrylamide was followed; however, DMF was used instead of THF/water and PMDETA was replaced by sparteine. The employed amounts were as follows: gold nanoparticles from 53 mg of tetrachloroauric acid, 0.3 mL of freshly distilled methyl methacrylate (2.8 mmol), 1 mL of DMF, 4 mg of CuBr (27.9 μ mol), and 12.7 μ L of sparteine (55.2 μ mol). This reaction was stirred at room temperature for 72 h.

The product was isolated by precipitation into methanol, centrifuged, and dried in vacuum. 160 mg of hybrid (54% monomer conversion) was obtained.

Cyanide Process To Remove Gold Cores from PNiPaam/PCyPaam Shell. 16 mg of gold–polymer hybrid was dissolved in 2 mL of THF, and 1 mL of water containing 20 mg of potassium cyanide was added. The mixture turned colorless upon shaking. The solvents were removed in vacuum, and the residue was treated with distilled THF. This THF solution was used for SEC analysis.

Cyanide Process To Remove Gold Cores from PMMA Shell. 59 mg of gold–polymer hybrid was dissolved in 2 mL of toluene. 25 mg of 18-crown-6 and 1 mL of water containing 40 mg of potassium cyanide were added. The mixture was regularly shaken and fresh air allowed to enter. The toluene phase was separated once it was colorless, and the resulting polymer was precipitated into methanol.

Amino Functionalization of Glass Slide. A commercial glass slide was cleaned by washing with detergent and rinsing and oxygen

plasma treatment; then, it was kept overnight in a 10% solution of (3-aminopropyl)triethoxysilane in dry THF. It was taken out if the solution, rinsed several times with THF, and stored in mQ-grade water.

Amino-Terminated Poly(ethylene oxide). PEO-NH₂ was prepared according to a literature procedure⁵¹ from PEO monomethyl ether with a molecular weight of 550 g/mol.

Grafting PEO-NH₂ to Au-5. Au-5 prepared from 5.5 mg of tetrachloroauric acid trihydrate (containing ~ 2 μ mol of active esters) dissolved in 1 mL of ethyl acetate was combined with a solution of 23 mg (41.8 μ mol) of PEO₅₅₀-amine in 1 mL of water. The two-phase mixture was stirred at room temperature overnight.

Reaction of Au-5 with Isopropylamine. Au-5 prepared from 11 mg of tetrachloroauric acid trihydrate (containing ~ 4 μ mol of active esters) was dispersed in 1 mL of THF, and 30 μ L of isopropylamine (350 μ mol) was added. The mixture was stirred at room temperature overnight, and the solvent and excess amine were removed in vacuum.

Results and Discussion

The protocol by Schiffrin and Brust is excellent for the synthesis of AuNP stabilized with nonpolar ligands such as alkylthiols. However, when employing functional thiols or disulfides as ligands, for example those carrying ester bonds, an immense difficulty to remove the excess phase transfer agent from the product disfavors this process. On the other hand, the method by Yee et al. avoids the use of a phase transfer salt but requires lithium triethylborohydride, an aggressive reducing agent, which reduces many chemical functional groups including ester bonds of disulfide ligands.

Ethyl acetate (EA) is an expedient solvent for gold nanoparticle synthesis as it is polar enough to dissolve tetrachloroauric acid but is not miscible with water. Therefore, we conducted a two-phase reduction of auric acid with a disulfide ligand present in the organic phase using an excess of aqueous sodium borohydride as a very mild reducing agent. Washing the organic layer thoroughly with water eliminates the excess of reducing agent, and as a consequence only the reduction of auric acid to gold nanoparticles occurs, while functional ligands are not attacked. As a result, gold nanoparticles protected by the ligands can be obtained in organic solvents in a direct way.

Following this procedure, several ligands have been explored during the synthesis of gold nanoparticles. Thiols have been used as commercially available, while disulfide ligands had to be synthesized. Disulfide ligands with C6 spacers were synthesized with different functional end groups. A 2-bromoisobutyrate moiety was used for the initiation of an atom transfer radical polymerization (ATRP).⁵² Pentafluorophenyl esters were used because of their high reactivity toward amines.⁵³ An acetate ligand was prepared to serve as a reference system as these moieties do not react with amines under mild conditions. The synthesis followed a general scheme. The disulfides **2** and **3** were synthesized by conversion of 1-mercapto-6-hexanol into the

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Table 1. Summary of Ligands Used for the Synthesis of Gold Nanoparticles

ligand	AuNP	size distribution	$\lambda_{\text{(UV-Vis)}}_{\text{max}}$
dodecylthiol	no	--	--
1-mercapto-6-hexanol	no	--	--
1-mercapto-11-undecanol	no	--	--
1 $\left(\text{HO} \text{---} \text{C}_{10} \text{H}_{21} \text{S} \right)_2$	no	--	--
2 $\left(\text{Br} \text{---} \text{C}(\text{CH}_3)_2 \text{---} \text{C}(=\text{O}) \text{O} \text{---} \text{C}_6 \text{H}_{13} \text{S} \right)_2$	Au-2	$2.89 \pm 0.94 \text{ nm}$	519 nm
3 $\left(\text{C}(=\text{O}) \text{O} \text{---} \text{C}_{10} \text{H}_{21} \text{S} \right)_2$	Au-3	$3.01 \pm 1.25 \text{ nm}$	517 nm
4 $\left(\text{HO} \text{---} \text{C}(=\text{O}) \text{C}_6 \text{H}_{13} \text{S} \right)_2$	no	--	--
5 $\left(\text{F}_5\text{C}_6\text{O} \text{---} \text{C}(=\text{O}) \text{C}_6 \text{H}_{13} \text{S} \right)_2$	Au-5	$2.92 \pm 1.06 \text{ nm}$	528 nm

^a All reactions have been performed in a water/ethyl acetate suspension with 9.7 mM auric acid, a sulfur-to-gold ratio of 0.9:1, and 1.1 M NaBH₄.

respective disulfide, followed by an esterification using either 2-bromoisobutyryl bromide or acetoxy chloride. The disulfide **5** was synthesized by esterification of bis(5-carboxypentyl) disulfide, which was successfully prepared starting from 6-bromohexanoic acid.

For the synthesis of gold nanoparticles auric acid and the respective ligand were dissolved in ethyl acetate. After addition of aqueous sodium borohydride, the formation of gold nanoparticles occurred within seconds, apparent by a color change from orange-yellow to dark-brown. Table 1 summarizes the results of different ligands used during the synthesis of gold nanoparticles. When thiols (such as dodecylthiol, 1-mercapto-6-hexanol, or 1-mercapto-11-undecanol) were employed, often a brown flocculation occurred before the addition of the reducing agent. The attempt to synthesize gold nanoparticles by using bis(dodecyl) disulfide or disulfides **1** or **4** as ligands failed. The failure might be due to the in-situ formation of gold nanoparticles, which are not soluble in ethyl acetate (as an alkyl surface is strongly nonpolar) causing an irreversible aggregation. In case of the acid disulfide **4**, a deprotonation of the acid groups by borohydride is likely, which would result in a charged and therefore water-soluble ligand. A transfer into the aqueous phase is then likely to happen, which would expose any material to additional NaBH₄, resulting in an irreversible aggregation of the gold nanoparticles. However, employing the disulfides **2**, **3**, or **5** resulted in small, narrowly distributed gold nanoparticles.

A rapid addition of the reducing agent was crucial for the formation of monodisperse nanoparticles. Tetrachloroaurate is also soluble in water, and thus, when the reducing solution is injected, a small part of the gold crosses the phase separation and gets reduced in the aqueous layer where no

protecting disulfide is present. However, the insoluble black material that results from this side reaction could easily be filtered off. The total loss of gold could be calculated to be below 20 wt % by carefully collecting, drying, and weighing this black precipitate.

After filtration, the resulting dispersion of AuNP in ethyl acetate contained an excess of disulfide ligand. By a concentration step and a following precipitation of the AuNP dispersion into hexane, this excess as well as other low molecular weight side products could be removed successfully. For ligand **5**, cooling the hexane mixture down to -20°C was necessary before a separation of the AuNP by centrifugation was possible. The excess of ligand used during the synthesis of gold nanoparticles could be easily retrieved afterward, as shown in the Supporting Information by example of ligand **5**. ¹⁹F NMR spectra showed that separation of product and excess ligand by precipitation was successful, and it also indicated that no reduction of the disulfide ligands during the particle formation step occurred.

After decanting the colorless hexane, the remaining gold nanoparticles could be dried and stored for several days at room temperature without any sign of aggregation. They could always be redispersed easily in various organic solvents such as THF, acetone, DMF, hexafluoroisopropanol, isopropanol, dichloromethane, trichloromethane, or toluene. UV-vis spectra of the AuNP as synthesized in EA and after precipitation into hexane and redispersion into THF showed no change of the plasmonic band (see Supporting Information), demonstrating the stability of the obtained gold nanoparticles. Gold nanoparticle dispersions were stable at 4°C for at least several months.

In addition to the UV-vis spectra also TEM measurements demonstrated that no particle aggregation occurred during the preparation and precipitation steps. Parts a and b of Figure 1 show TEM images of gold nanoparticles prepared using ligands **2** and **5**, respectively. Gold nanoparticles stabilized with ligand **2** had a mean diameter of $2.89 \pm 0.94 \text{ nm}$, while gold nanoparticles stabilized with ligand **3** and **5** had a mean diameter of 3.01 ± 1.25 and $2.92 \pm 1.06 \text{ nm}$, respectively. Thus, the obtained nanoparticle sizes are comparable to those prepared by the Brust method.²⁹

To explore the application of functionalized gold nanoparticles, experiments to graft polymers from and onto gold nanoparticles have been performed. The different synthetic polymerization approaches are summarized in Scheme 1.

In order to graft polymers from gold nanoparticles, gold nanoparticles stabilized with ligand **2** have been investigated in a surface-initiated atom transfer radical polymerization (ATRP). As the gold-sulfur bond is not stable at elevated temperature⁴¹ if no excess ligands are present,⁵⁴⁻⁵⁶ the surface-initiated ATRP of *N*-isopropylacrylamide (Nipaam), *N*-cyclopropylacrylamide (Cypaam), and methyl methacrylate (MMA) was performed at room temperature. For the polymerization of Nipaam and Cypaam a water/THF mixture

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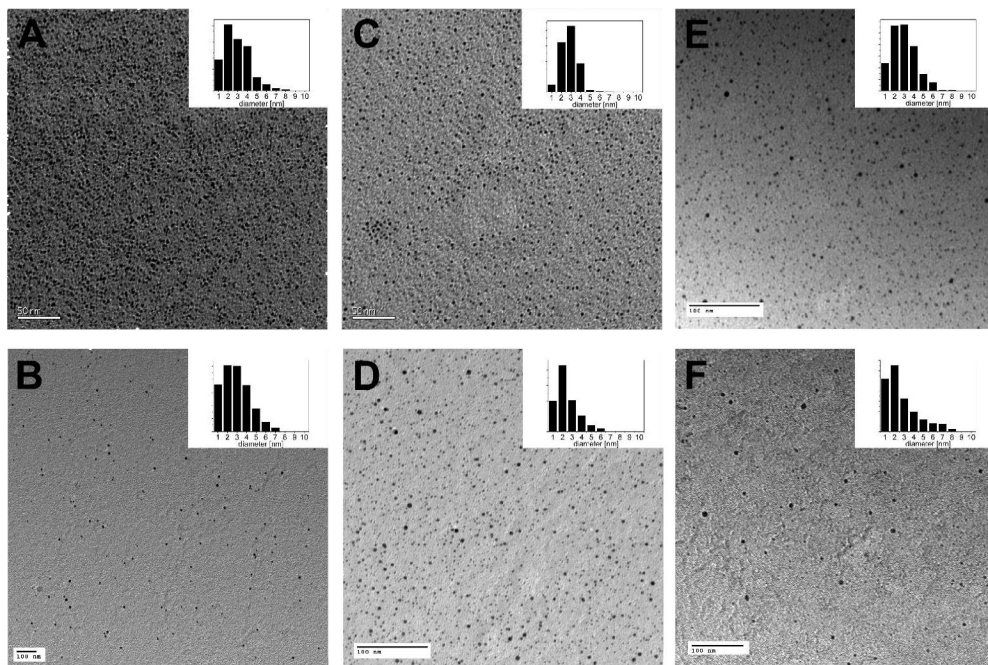
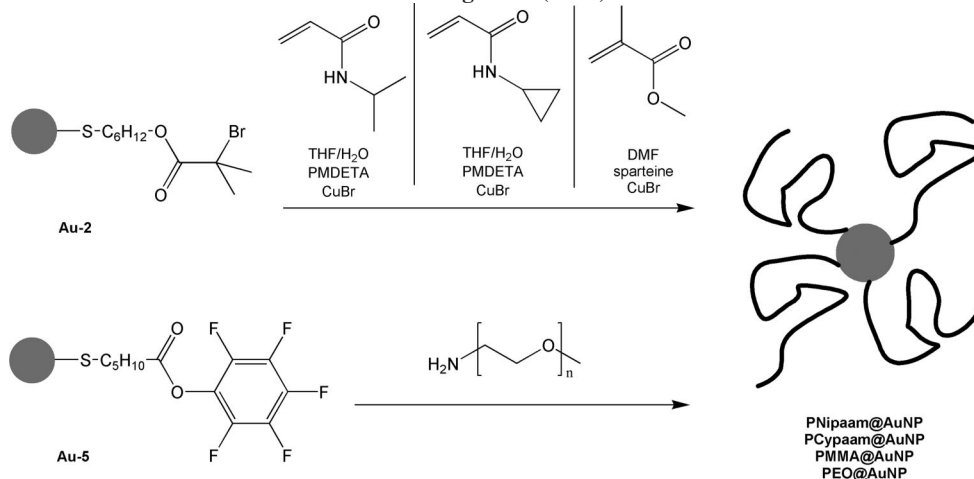


Figure 1. TEM images of gold nanoparticles synthesized by ethyl acetate method: (A) functionalized with ligand **2** (**Au-2**) and (B) with ligand **5** (**Au-5**). TEM images of polymer–gold hybrids prepared by grafting from **Au-2**: (C) PNipaam@AuNP, (D) PCypaam@AuNP, and (E) PMMA@AuNP. TEM images of polymer–gold hybrids prepared by grafting-onto **Au-5**: (F) PEO@AuNP. The scale bars have lengths of 50 nm (A, C) and 100 nm (B, D, E, F).

Scheme 1. Grafting-From: Polymerization of Nipaam, Cypaam, and MMA from Gold Nanoparticles Stabilized with Ligand 2 (Au-2); Grafting-onto: Attachment of Amino End-Functionalized PEO ($M_n = 550$ g/mol) onto Gold Nanoparticles Stabilized with Ligand 5 (Au-5)



was chosen as the solvent. Gold nanoparticles stabilized with ligand **2** could still be dispersed in this solvent mixture without sonication. In case of MMA, a solution of the monomer in THF seemed to be a bad solvent for AuNP as it caused irreversible nanoparticle aggregation. However, aggregation of the gold nanoparticles could be avoided if the polymerization was performed in DMF as the solvent. No sacrificial initiator was used in any of the polymerizations.

No obvious color change occurred during the polymerization of Nipaam, Cypaam, or MMA, which indicated that the gold particles did not aggregate during the polymerization (see Supporting Information). This was confirmed by TEM measurements. Figure 1C–E shows the TEM images of gold nanoparticles grafted with PNipaam (Figure 1C), PCypaam (Figure 1D), or PMMA (Figure 1E). Careful analysis of the diameter of the gold nanoparticles revealed that there was

no significant change of diameters of particles before and after polymerization.

The polymer–gold hybrid could be dried and redissolved, as the polymeric shell dictates the solution properties of the polymer–gold hybrids; i.e., precipitation occurred in poor or bad solvents for the polymer (e.g., PCypaam@AuNP: hexane, diethyl ether, and THF), while the gold particles could be dispersed in good solvents for the polymer (e.g., PCypaam@AuNP: water, DMF, DMSO, and CHCl_3). While the initiator-coated nanoparticles were not soluble in water, gold nanoparticles grafted with either PNipaam or PCypaam chains could be completely dissolved in water, if the temperature was below their lower critical solution temperature. Thus, ^1H NMR spectra of dispersed PNipaam@AuNP and PCypaam@AuNP have been recorded in D_2O (see

Supporting Information), and they do not differ from those polymerized in solution.

The resulting polymer–gold hybrids differed in size of the polymer shell dramatically. This was investigated by thermogravimetric analysis (TGA) in combination with size exclusion chromatography (SEC). PNipaam@AuNP consisted of 20 wt % gold, while PMMA@AuNP consisted only of 5.5 wt % gold as determined by TGA (see Supporting Information). These values matched with the length of the polymer chains grafted from the gold nanoparticles. A sample of hybrid material was subjected to cyanide treatment, which dissolved the gold cores and detached the polymer chains that had been grafted from the surface. SEC measurements of the polymers after cyanide treatment of the polymer–gold hybrids gave a peak molecular weight for the grafted PNipaam chains of 9500 g/mol, while a peak molecular weight of 130 000 g/mol was measured for grafted PMMA. Both SEC curves were monomodal and showed a narrow molecular weight distribution ($M_w/M_n < 1.14$ for PNipaam), indicating that all chains grew under the same controlled conditions. Taking the size of the gold nanoparticles into account, the number of polymer chains per square nanometer could be calculated (see Supporting Information). For PMMA@AuNP a value of 0.75 chains/nm² was calculated, while for PNipaam@AuNP 2.2 chains/nm² was obtained. These values are in the same range as literature reports on grafting-to densities, e.g. 0.94 chains/nm² for 13.3K polystyrene^{43b} or 2.2 chains/nm² for 4.7K PNipaam,³⁴ but are higher than the literature value for PMMA@AuNP of 0.3 chains/nm² reported for grafting-from density by Ohno et al.⁴¹ They used a one-phase reduction method of auric acid with NaBH₄ in methanol, exposing the functional ligand to NaBH₄ for a longer time, which may result in a partial reduction of the ester.

Further, the stimuli-responsive behavior of the polymer–gold hybrids PNipaam@AuNP and PCypaam@AuNP in water was investigated. Turbidity measurements of the hybrids revealed a lower critical solution temperature (LCST) of 32 °C for PNipaam@AuNP and 48 °C for PCypaam@AuNP. The turbidity measurements are in full agreement with UV–vis measurements, which show an increase of the intensity of the plasmon band around LCST, possibly due to scattering. As an example, the turbidity at 633 nm and UV–vis absorption data at 400 nm have been plotted as a function of temperature in Figure 2. The black squares represent the turbidity data and the gray circles the UV–vis data. Clearly, both measurements show a sharp transition at 32 °C due to the coil–globule transition of the PNipaam chains, which is in accordance with the LCST in water found for PNipaam attached to gold surfaces.^{22,46} Similar results were found for the determination of the LCST of PCypaam@AuNP where the LCST occurred at 48 °C, in agreement with the LCST of free PCypaam at 49 °C, as reported in the literature.⁵⁷

In addition to the described grafting-from experiments using **Au-2**, we also conducted grafting-onto experiments

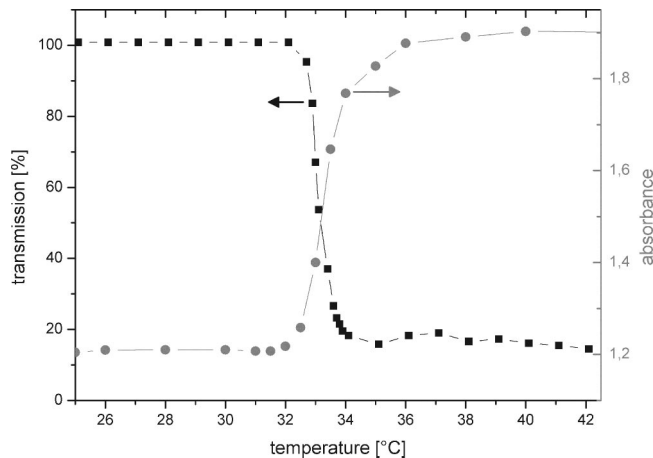


Figure 2. Determination of the lower critical solution temperature of PNipaam@AuNP by measuring the turbidity at 633 nm and the UV–vis absorption at 400 nm as a function of temperature.

utilizing the reactive coated **Au-5**. Pentafluorophenyl esters have proven to be extremely useful in organic and especially polymer science as they react quantitatively with amines under very mild conditions.⁵³ Thus, utilizing these reactive functions as ligands for gold nanoparticles opens new synthetic routes for the functionalization of gold nanoparticles. As highlighted in Scheme 1, we investigated the reaction of such pentafluorophenyl ester-functionalized gold nanoparticles (**Au-5**) with amino end-functionalized poly(ethylene oxide) ($M_n = 550$ g/mol). Hence, **Au-5** dispersed in ethyl acetate was stirred with an aqueous solution of amino end-functionalized poly(ethylene oxide). A successful reaction occurred, which could easily be observed by a complete transfer of the gold nanoparticles into the water phase (see Figure 3a). Recording FT-IR spectra before and after the reaction of **Au-5** with isopropylamine confirmed a complete conversion of all active ester groups into the respective amide groups, as shown in Figure 3b. Before the reaction the prominent band for the C=O group of the pentafluorophenyl ester was observed at 1783 cm⁻¹ along with the band for the aromatic ring of the pentafluorophenyl ester at 1516 cm⁻¹. After the conversion, these two bands vanished completely, and only the bands for a primary amide at 1639, 1546, and 3286 cm⁻¹ could be detected, proving the successful and complete conversion. The observation of amide bands also indicates that an exchange of the sulfide ligands against an amino ligand did not happen. The dried isopropylamide-functionalized material could easily be re-dispersed in THF.

Gold nanoparticles featuring reactive functionalities on their surface, such as pentafluorophenyl esters, can also be used as nanobuilding blocks for the formation of nanoparticle polymer hybrid multilayers on the basis of covalent bonds. For this purpose, an amino-functionalized glass slide was immersed into a dispersion of the active ester covered gold nanoparticles **Au-5** for 20 min. Immersion for a longer time (12 h) did not result in the deposition of any further nanoparticles. After rinsing with THF and water, the slide was immersed into a 1 wt % solution of polyallylamine ($M_n = 65$ 000 g/mol) in water for 20 min and then rinsed with water and THF again. This cycle was repeated several times.

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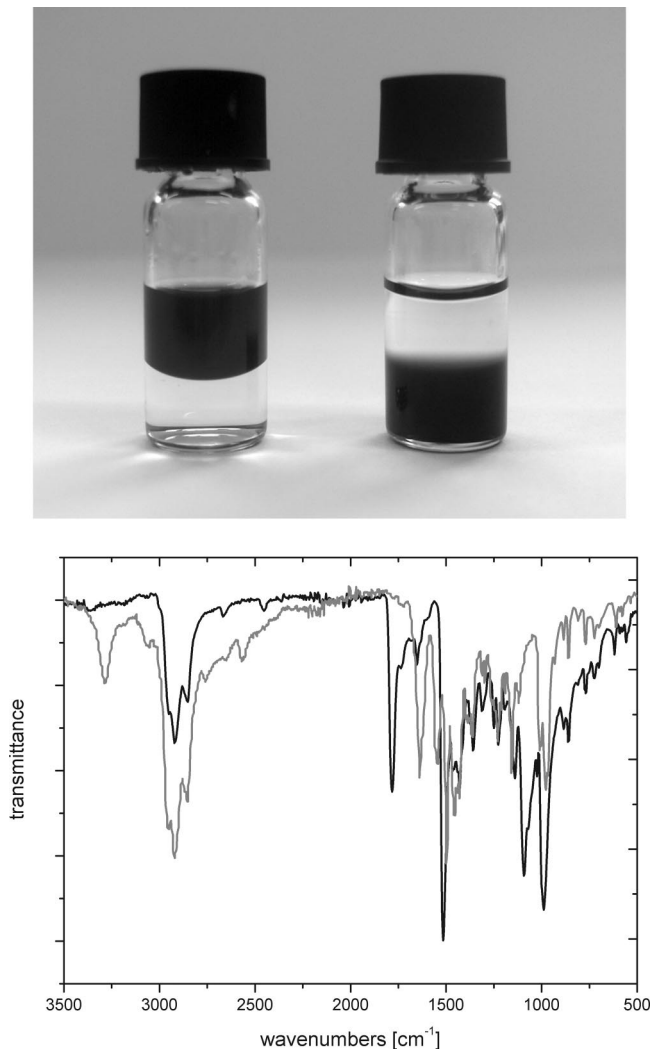


Figure 3. (a) Pentafluorophenyl ester-functionalized gold nanoparticles, **Au-5**, dispersed in ethyl acetate (upper phase) floating over a water phase (left vial). After addition of amino-functionalized PEO, all gold nanoparticles are transferred from the ethyl acetate phase into the lower water phase (right vial). (b) FT-IR spectra of pentafluorophenyl ester-functionalized gold nanoparticles, **Au-5** (black line), and after reaction with isopropylamine (gray line).

After the deposition of each layer a UV-vis absorption spectrum was recorded. With an increasing number of attached layers, the absorption and the plasmon band evolving around 540 nm increased. In Figure 4, the absorption at 510 nm is plotted against the number of layers. With each deposition cycle the absorption increased, and after the second gold nanoparticle layer a linear increase of the absorption with the number of deposited layers could be observed. In a control experiment with gold nanoparticles functionalized with acetate groups, **Au-3**, no multilayer formation could be realized. Accordingly, the active ester groups on the surface of the gold nanoparticles are essential in order to facilitate a multilayer formation with polyallylamine.

Conclusion

We presented a new and versatile method for the synthesis of functionalized gold nanoparticles in an organic solvent

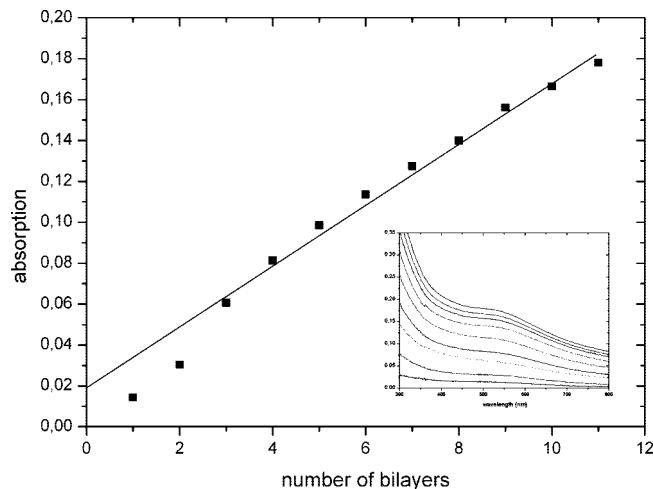


Figure 4. UV-vis spectra taken after different adsorption cycles during the preparation of an **Au-5**/polyallylamine multilayer (inset) and plot of the absorbance of the plasmonic band at 510 nm versus the number of bilayers deposited.

employing a two-phase reduction with ethyl acetate and water. The method features several advantages: It can be applied without the use of a phase transfer agent. Also, the reducing conditions are mild enough to utilize functional disulfide ligands, for example, those exhibiting 2-bromoisobutyrate, acetate, or pentafluorophenyl ester functionalities. The obtained gold nanoparticles can be precipitated and redispersed without any irreversible aggregation occurring.

Stimuli-responsive polymers were grafted from the surface of 2-isobutyrate-covered gold nanoparticles, and the resulting polymer gold hybrids showed the plasmonic band of the gold core and the lower critical solution temperature of the polymeric shell. On the other hand, gold nanoparticles covered with pentafluorophenyl esters could be used to graft amino end-functionalized poly(ethylene oxide) onto them. Additionally, these gold nanoparticles featuring a reactive functionality could successfully be used in the preparation of multilayers on the basis of covalent bonds between gold nanoparticles and polyallylamine.

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Supporting Information Available: ¹⁹F NMR spectra of **5** and **Au-5**, UV-vis absorption spectra of **Au-2** and PNipaam@AuNP, ¹H NMR spectra of PNipaam@AuNP and PCypaam@AuNP, thermogravimetric data of PMMA@AuNP and PNipaam@AuNP, and an exemplary graft density calculation. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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