


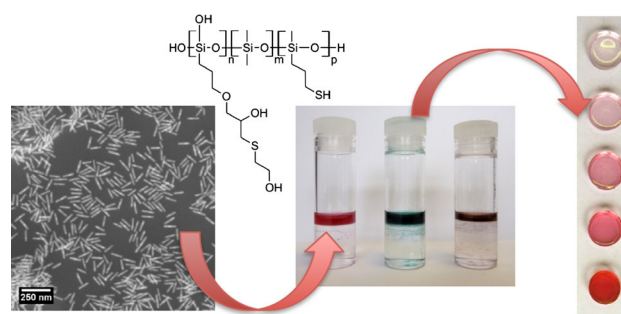
Controlled surface modification of gold nanostructures with functionalized silicon polymers

Denis Chateau¹ · Adrien Liotta¹ · Damia Gregori¹ · Frederic Lerouge¹ ·
Frederic Chaput¹ · Anthony Desert¹ · Stephane Parola¹ 

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Abstract The stabilization of metal nanoparticles using surface modification has been intensively investigated. We propose an alternative to the use of surfactants, long-chain polymers or silica shells in order to provide easy and efficient stabilization of a wide range of metallic nanostructures. The prepared silicon oligomers were characterized, optimized and successfully used for surface modifications of nanospheres, nanobipyramids, nanorods of both gold and silver. The modified nanoparticles were then easily incorporated into monolithic sol-gel materials based on silica. This original route toward hybrid composite was efficiently used to prepare composite sol-gel materials with plasmonic nanostructures for optical applications.

Graphical Abstract Specifically designed silicon polymers are used to efficiently stabilize metal nanoparticles and allow homogeneous dispersion into sol-gel materials.



Keywords Silicon · Gold · Surface functionalization · Metal nanoparticles · Sol-gel · Plasmon

1 Introduction

Surface modification of metal nanoparticles has been investigated for a long time with the aim to either contribute to the stability of the colloids or to achieve new functionalities such as fluorescence or molecular recognition. Incorporation of metal nanoparticles in transparent glass [1, 2] or polymers [3, 4] has also been investigated for optical application but remains complicated due to particles instability during the preparation process, and to a difficult control of the shape/size of the nanostructures. In situ growth of metal nanoparticles in glass matrices can be achieved through several processes such as laser, thermal or chemically induced growth but remain limited to mostly spherical nanoparticles or wires-type nanostructure and generally with poor homogeneity [1–22]. The use of

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✉ Stephane Parola
stephane.parola@univ-lyon1.fr

¹ Laboratoire de Chimie, UMR 5182, Université de Lyon, Ecole Normale Supérieure de Lyon, CNRS, Université Lyon 1, 46 allée d'Italie, 69364 Lyon, France

polymers for colloidal stabilization has already been described in the case of metal nanoparticles and in particular gold nanoparticles (AuNPs). Thus, various systems have been studied such as thiolated polyethyleneglycol (PEG-SH) [23–26], polyelectrolytes [27–29], polyelectrolytes combined with silica shell and hydrophobation using octadecyltrimethoxysilane [30], mercaptosuccinic acid followed by TOAB [31] or mercaptopropyltrimethoxysilane followed by hydrophobation by octadecyltrimethoxysilane [32]. Despite the important amount of studies, the obtained systems are either complicated to achieve or do not offer the desired stability in organic solvent allowing their use during sol–gel process.

We propose an original approach, which involves the surface modification of metal nanoparticles of various shapes and sizes using a functional thiolated silicon polymer. This polymer acts as a stabilizing agent of the colloids both in wide range of solvent and in transparent glass materials using the sol–gel process. In this paper we intend to develop the synthesis and optimization of the silicon polymer structure and the surface modification of gold nanostructures.

2 Experimental details

2.1 Synthesis of silicon polymer P1

8.3 mL (46.95 mmol) of diethoxydimethylsilane, 760 μL (4.18 mmol) of (3-mercaptopropyl)-methyl-dimethoxysilane and 780 μL (3.62 mmol) of (3-glycidoxypropyl)-methyl-dimethoxysilane (GLYDMO) were mixed together in a round bottom flask, equipped with a condenser, containing 4 mL MilliQ water and 40 μL HCl (0.1 M). After 20 min of stirring at room temperature, 380 μL of triethylamine (2.7 mmol) was added. The mixture was then refluxed at 65–70 $^{\circ}\text{C}$ for 2 h. Finally, the condenser was replaced with a distillation apparatus, 10 mL of ethanol was added and the mixture heated at 120 $^{\circ}\text{C}$ until all the solvents were removed. The final residue is dispersed in ethanol (30 mL) for storage.

^1H NMR (300 MHz, CDCl_3) δ 3.92–3.81 (m, \approx 1H), 3.59–3.43 (m, \approx 2H), 3.50–3.38 (m, \approx 2H), 2.74–2.56 (m, \approx 2H), 2.65–2.46 (m, \approx 2H), 1.81–1.53 (m, \approx 4H), 1.33 (t, $J = 7.1$ Hz, \approx 0.3 \times 1H), 0.72–0.54 (m, \approx 2H), 0.60–0.41 (m, \approx 2H), 0.19–0.02 (m, \approx 6H + 13 \times 6H). ^{29}Si NMR (99 MHz, Acetone) δ –13.62 (D1 OH), –14.18 (D1 OH), –14.98 (D1 OH), –19.19 (cycles D4), –21.93 to –22.21 (D2), –22.83 (D2).

2.2 Synthesis of silicon polymer P2 (with n and p around 0.1)

The synthesis was achieved in two steps.

2.2.1 Coupling of GLYMO with 2-mercaptoethanol

619 μL (2.8 mmol) of (3-glycidoxypropyl)trimethoxysilane, 199 μL (2.8 mmol) of 2-mercaptoethanol and 500 μL of methanol were mixed together in a 5 mL vial filled with argon. After the addition of 12.5 μL (0.1 mmol) of TMG (tetramethylguanidine), the mixture was stirred and heated 5 min at 60 $^{\circ}\text{C}$ and let cool down to RT for 30 min. The completion of reaction was checked by IR analysis (disappearance of epoxy bands around 900 cm^{-1}).

2.2.2 Synthesis of polymer P2

500 μL (2.8 mmol) of (3-mercaptopropyl)-methyl-dimethoxysilane, 550 μL of MilliQ water and 50 μL of 0.1 M HCl solution were mixed together under vigorous stirring in a round bottom flask, equipped with a condenser. After 10 min, 4.1 mL (23.2 mmol) of diethoxydimethylsilane was added to the mixture. Finally, after 10 min, the modified GLYMO mixture and 380 μL (3.3 mmol) of TMG were added to the flask. The mixture was then refluxed at 120 $^{\circ}\text{C}$ for 3 h. Finally, the condenser was replaced with a distillation apparatus, until all volatiles were removed. The residue was dispersed in diethylether (20 mL), washed briefly with 10 mL of water, dried on MgSO_4 and concentrated. The final viscous liquid was diluted into 20 mL of ethanol for storage.

^1H NMR (300 MHz, CDCl_3) δ 3.92 (m, \approx 1H), 3.77 (t, $J = 6.9$ Hz, \approx 2H), 3.45 (m, \approx 4H), 2.78 (m, \approx 2H), 2.68 (m, \approx 2H), 2.53 (m, \approx 2H), 1.64 (m, \approx 4H), 1.33 (t, $J = 7.1$ Hz, \approx 1H), 0.62 (m, \approx 2H), 0.52 (m, \approx 2H), 0.14–0.02 (m, \approx 6H + 8 \times 6H). ^{29}Si NMR (99 MHz, CDCl_3) δ –10.9 to 12.8 (D1 OH), –19.0 (D4 cycles), –20.7 to –23.1 (D2), –65.4 to 68.6 (T3).

2.3 Functionalization of nanoparticles

2.3.1 Quick functionalization of nanoparticles for THF extraction process

The gold nanobipyramids and nanospheres were prepared as described in our previous articles [33–36] and freshly purified by centrifugation (8000 rpm, one time) followed by redispersion in 5 mM CTAB at a concentration of 0.25 mM Au^0 .

Typically, 1 mL of those nanoparticles were mixed with 25 μL of an ethanolic 1 % solution of P2 (made with $n = 0.08$ and $m = 0.1$) and sonicated for 30 s in a sonic bath. 1 mL of THF was added to the mixture with manual stirring, followed by 225 μL of diethyl ether. The stirring was continued for five seconds, and then, the phase separation occurred. The water phase can be removed easily using a glass pipette. The organic phase can be diluted two times in THF for storage.

2.3.2 Functionalization of nanoparticles with isolation by centrifugation

4 mL of gold or silver nanoparticles (at 0.25 mM [Au⁰] or [Ag⁰] in 2 mM CTAB or CTAC) was mixed with 100 μ L of an ethanolic 1 % solution of **P2** (made with $n = 0.1$ and $m = 0.1$), sonicated for 5 min in a sonic bath. The mixture was incubated for at least one hour (up to 18 h for the bigger particles) at 50 °C. After centrifugation (8000 rpm), the particles were redispersible using a sonic bath in ethanol, acetone and THF.

3 Results and discussion

The design and synthesis of silicon-based polymers was investigated in order to (1) stabilize the gold nanoparticles in wide range of solvents and (2) overcome the instability of gold nanoparticles in sol–gel media during the formation of monolithic transparent metal doped materials.

Typically, transparent silica-based composite materials are prepared using MTEOS-based sols diluted in tetrahydrofuran (THF) [37–40]. For the present study, the selected nanoparticles possess different geometries, either anisotropic in the case of gold bipyramids or isotropic gold nanospheres. Both systems are prepared in cationic surfactants media, which make them difficult to stabilize efficiently in organic solvents such as THF. One efficient way to stabilize the AuNPs in the sol–gel media is to coat the surface of the particles with a silica shell. Unfortunately the synthesis is not always easily controlled (silica layer homogeneity) and time consuming, and the particles shape can be affected during the coating process [30, 41]. We decided to develop a new series of silicon-based polymer, which will bring strong affinity of the covered particles for the sol–gel media, and bearing thiol pending groups ensuring efficient surface grafting on the metal.

The preparation of linear functional silicon polymers can be achieved by simply mixing different alkoxy silanes monomers that can be selectively hydrolyzed together or separately in order to obtain the desired oligomers. It is important to note that for this study, the polymer length did not need to be perfectly controlled in order to improve the particle stabilization.

Since gold particles are prepared in water-based solutions, the polymers have to be compatible with such environment for efficient grafting. The first attempts to functionalize AuNPs in water with 3-mercaptopropylsilanes and diethoxydimethylsilane (DEDMS)-based polymers were unsuccessful. The main reason was because of the bad compatibility between the polymer and the water dispersion of AuNP. Therefore, an epoxy-silane, (3-glycidoxypropyl)methyl dimethoxysilane (GLYDMO), was added to increase the hydrophilicity of the

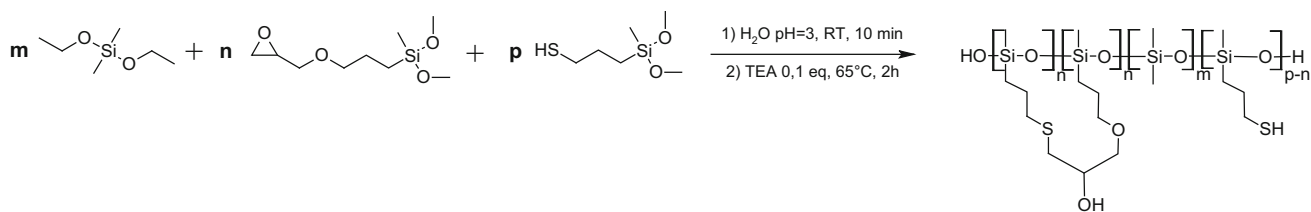
polymer and consequently improve the homogeneous mixing. The preparation of polymer **P1** is shown in scheme 1. It was prepared and used for particle functionalization such as previously reported [40]. Unfortunately, despite its good compatibility with the particles solution, **P1** led to dispersion showing low stability, in particular in THF, after few days of storage. Moreover, the reactivity toward the metal surface was sometimes too low (especially for gold nanospheres).

We assumed that to overcome this lack of reactivity and to improve the time stability, higher amount of thiol units were needed together with hydroxyl functions along the polymer chain. Indeed, coupling between the mercaptopropyl units and the epoxy occurred during the reaction leading to a lower amount of available thiols for anchoring on the AuNPs. We thus designed a system derived from **P1**, with several important changes. Prior to its inclusion within the polymer, the epoxy-silane was reacted with 2-thioethanol to avoid coupling on the MPDMS during the synthesis. Using this approach, more thiols were available from the mercaptopropyl units, the hydrophilicity was high and the beta-hydroxysulfide groups were still present. The GLYDMO precursor was replaced by (3-glycidoxypropyl)trimethoxysilane (GLYMO) in order to compensate the loss of epoxy/thiol crosslinking. The (3-mercaptopropyl)-methyl-dimethoxysilane (MPDMS) was hydrolyzed alone, to favor the formation of oligo-mercaptopropylsilicone blocks inside the final polymer chains. Finally, TEA was replaced with the way more basic tetramethylguanidine (TMG). Less water was used, which made the control of the chain length easier. The polymer **P2** was thus obtained in two steps (Scheme 2). This polymer showed much higher reactivity toward AuNPs, which reduced the time of functionalization and increased considerably the stability of the dispersions in the final media.

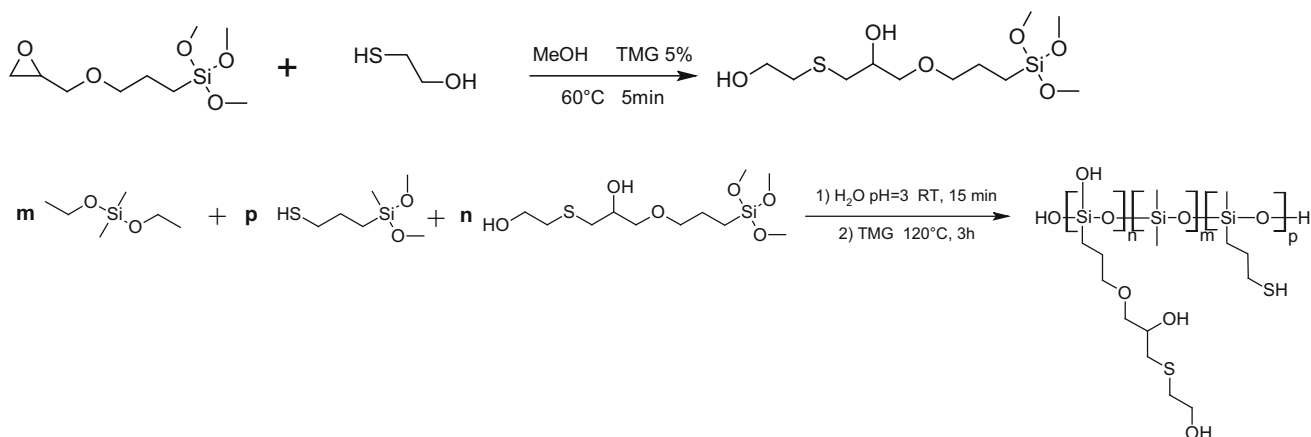
The reactivity and stabilizing efficiency of the new **P2** polymer was evaluated on several kinds of metallic nanoparticles exhibiting different geometries such as gold bipyramids, silver nanorods and gold nanospheres. Efficient grafting was evidenced on anisotropic particles by electronic microscopy. Figure 1 shows the polymer shell thickness covering gold bipyramids of different length. In the case of silver nanorods, aggregation was observed with non-grafted systems. Functionalized rods did not exhibit any packing (Fig. 2).

Interestingly, condensation between silanol groups along **P2** could increase both the polymer chain length and densification of the shell surrounding the nanoparticles. As a direct consequence, the shell thickness could be controlled by varying the reaction time between the nanoparticles and the polymer. Figure 1 shows the impact of the reaction time on the thickness of the final shell.

Efficiency of grafting was also evidenced through solvent extraction of the particles from water to THF (Fig. 3). The metallic colloids in a surfactant/water mixture were



Scheme 1 Synthesis of the polymer **P1**



Scheme 2 Synthesis of polymer **P2**

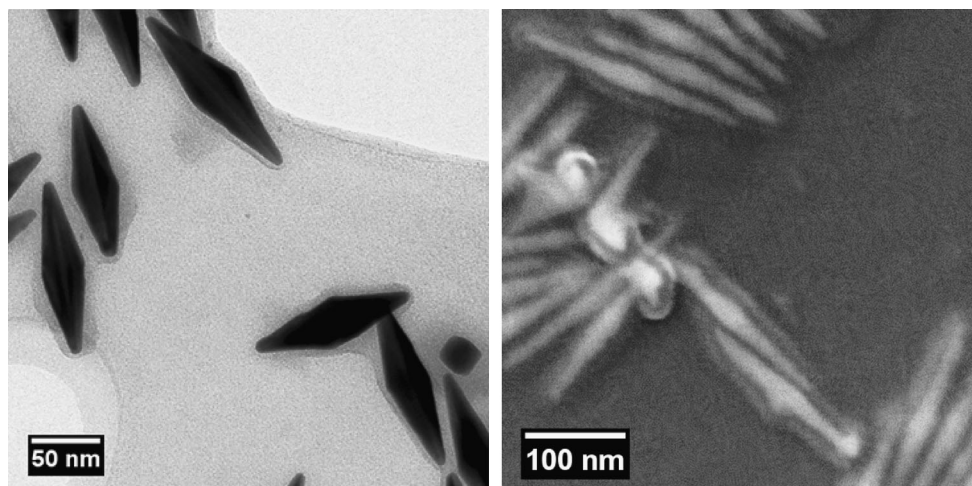


Fig. 1 *Left* Transmission electron microscopy (TEM) photograph of gold nanobipyramids freshly functionalized with **P2**. 1 mM of NiNO_3 was introduced in the particle solution to enhance polymer contrast. The particles were in contact with the polymer for one night before

isolation by centrifugation. *Right* Scanning electron microscopy (SEM) imaging of 6-month old water dispersion of functionalized nanobipyramids showing the important growth of the thick shell

incubated with either **P1** or **P2** for different durations. THF was then added, followed by a small amount of diethyl ether leading to two different phases. The organic phase was quickly separated from water and became the same color as the previous particles suspension. Moreover, the surfactant/water mixture became colorless proving that all the polymer-functionalized particles were extracted from the aqueous

phase to the organic one (Fig. 3). The higher reactivity of **P2** compared to **P1** was evidenced by the faster incubation time from few minutes to few hours, respectively.

The THF phase was easily recovered, concentrated by evaporation and stored. Such suspension could be used directly to prepare AuNPs containing sol-gel materials (Fig. 4) [40].

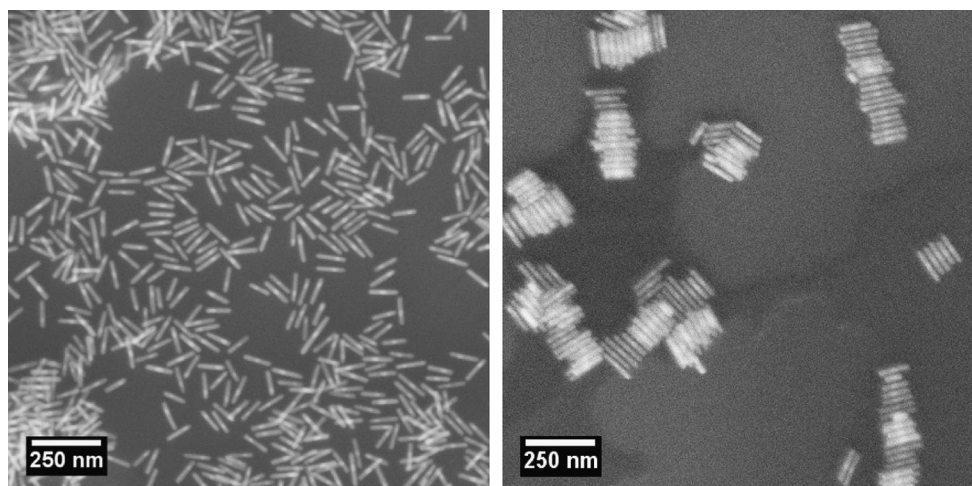


Fig. 2 Surface modification of silver nanorods showing the high dispersibility with polymer (*left*), while without polymer it showed important self-assembling aggregation (*right*)

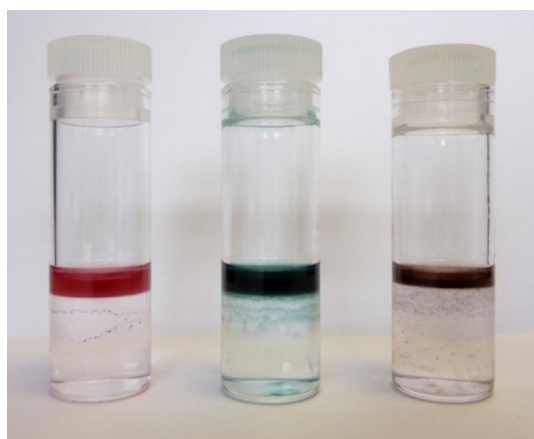


Fig. 3 Efficient extraction and stabilization into THF phase (*top*) versus aqueous phase (*bottom*) of 40 nm gold nanospheres (*left*), 40 × 23 nm gold bipyramids (*middle*) and 85 × 26 nm gold bipyramids (*right*) using **P2**

The ratio between the different monomers during polymer synthesis is a way to control the reactivity and the compatibility of the polymer with the organic solvent. The

amount of opened epoxy units (n) mostly control the polarity and the reticulation of the polymer. For the THF extraction, polymers with a low polarity (with $0.05 < n < 0.08$ and $p = 0.1$) are better, despite being less soluble in water. When the particles are redispersed in ethanol, after centrifugation, a polymer with $n = p = 0.1$ gives better results. Therefore, one can tune easily the behavior and the solvent compatibility of the final particles by changing the amount of polar crosslinking units in the polymer backbone.

The spectroscopic characterization on the modified nanoparticles showed no broadening, but only a little shift of the absorption band when transferred from water to THF, in particular for anisotropic bipyramids for which the spectrum is mostly affected on the longitudinal resonance (Fig. 5). The most important shift is observed in the case of the more elongated bipyramids. Such behavior, attributed to the sharpness of the tips, was already described in previous work [33]. Similarly, when transferred into the sol-gel silica materials, no broadening of the absorption band was observed demonstrating the quality and homogeneity of the dispersion in the solid phase [40].

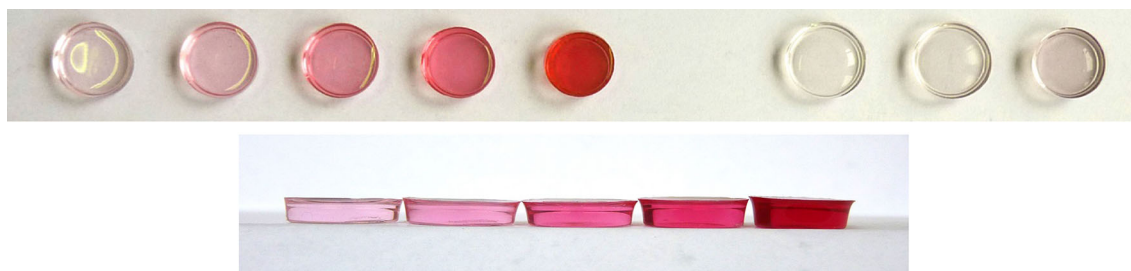


Fig. 4 Example of dispersion of 45 nm gold nanospheres (*top left*, respective concentrations from left to right 0.03, 0.06, 0.13, 0.25, 0.5 mM in Au⁰) and gold nanobipyramids (*top right*, respective concentrations from left to right 0.06, 0.13, 0.25 mM in Au⁰) at

various concentrations in sol-gel silica-based materials. Side view of the materials with gold nanospheres (*bottom*). The diameter of the prepared xerogels is 1 cm

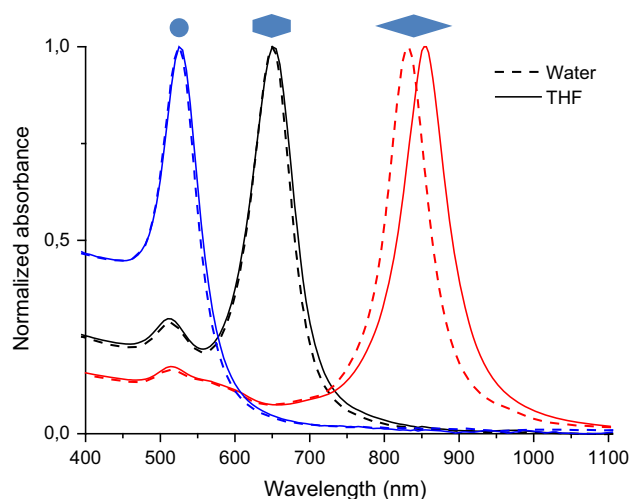


Fig. 5 UV-vis spectra of various gold nanoparticles in water (*dot line*) and in THF (*full line*) after solvent extraction with the polymer **P2**. The particles used were respectively 45 nm gold nanospheres, 40 × 23 nm gold bipyramids and 105 × 0 nm gold bipyramids from left to right

4 Conclusion

As a conclusion, we were able to design a new silicon-based polymer, which allowed easy and efficient surface functionalization of metal nanoparticles of different size and shape. This surface modification allowed important stabilization of the nanoobject in suspension and furthermore permitted their transfer in organic solvents such as THF for further use. Such approach is extremely convenient for the preparation of very thin layer of silicone at the surface of any metal nanoobject and even allows a good control of this thickness together with easy processing. As demonstrated by our group, this strategy gave the opportunity to prepared for instance sol-gel-based monoliths or films with incorporation of metallic nanostructures of controlled shape and size with highly homogeneous dispersion. This opens the route toward new plasmonic hybrid materials for fundamental investigations on the understanding of charge and energy transfers and further devices for enhancement of optical responses in sensors, optical filters or imaging technologies. By changing the nature of the monomers, for example using aminosilanes, the polymer was also adapted to other systems such as rare-earth fluoride or oxide nanoparticles.

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