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Asymmetrically Functionalized Gold Nanoparticles Organized in One-Dimensional Chains

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ABSTRACT

Organized assembly remains a major challenge for optimizing and extending the application of nanoparticles. Here we report a simple method to assemble spherical gold nanoparticles (AuNPs) in one-dimensional (1D) chains. The chain-forming process takes advantage of asymmetrically functionalized AuNPs that serve as building blocks. The 1D AuNP chains were prepared by covalent attachment of spatially localized functional groups on the AuNPs to polymer backbone pendent groups. We demonstrate control of interparticle spacing and the preparation of 1D chains containing AuNPs of different sizes.

Substantial efforts have been put into investigations of metal nanoparticles due to their unique localized surface plasmon resonance (LSPR) properties[1−3] and their application in plasmonics,[4] photonics,[5] surface-enhanced spectroscopies,[6] and device fabrication.[7] Specifically, AuNPs have been used in optical and electronic detection systems[8−10] and therapeutics.[11] To optimize and extend the application of metal nanoparticles, methods must be developed to control the assembly and organization of these materials. Assemblies of nanoparticles also provide optical and electronic properties that are distinct compared to individual particles or disorganized macroscale agglomeration.

One approach for organizing nanoparticles is to control the composition of the ligand shell around the particles. Typically the ligand shell plays an important role in imparting functionality for specific applications of metal nanoparticles. In most cases, ligands in the shell are selected to chemically define the nanoparticle surface for stabilization in different environments (e.g., aqueous or organic solvents) or to provide attachment sites for probe molecules for sensing applications. Several strategies for controlled assembly of AuNPs are based on tailoring the composition of the ligand shell. Most of these approaches have been based on limiting the number of reactive ligands in the shell to control the possible types of assemblies that can be formed.[12−15] An alternative approach is to limit the spatial distribution of reactive ligands to produce asymmetrically functionalized nanoparticles. In a recent report, we described a simple asymmetric functionalization technique used to produce AuNPs with reactive ligands localized on a small region of the AuNP surface. A major advantage of the asymmetric functionalization approach is that the ligands in a spatially limited region of the surface may be used for further chemistry and the rest of the ligands can be selected to remain unreactive during any coupling process. As an example, we prepared asymmetrically functionalized AuNPs and assembled the particles together to form dimers.[16]

In this letter, we demonstrate how these asymmetrically functionalized metal nanoparticles can be used as versatile building blocks for controlled organization by producing one-dimensional (1D) AuNP chains using a polymer as a template for assembly. The organization of AuNPs in 1D chains provides a way to tune the optical properties of the AuNPs. For example, several groups have shown that LSPR coupling between particles occurs in a nanoparticle chain in the near-field region[17] and that electromagnetic energy can propagate over a distance of a few hundred nanometers[18,19] to create a plasmon-based waveguide.[20] Organizing nanoparticles into 1D assemblies with controlled interparticle spacing should aid the development of nanoparticle-based components for miniaturized photonics devices.[4,21] The formation of well-organized nanoparticle-polymer composite materials also may have application in sensing and drug delivery.

Because of the challenges associated with organized assembly, few methods have been successful in the well-controlled formation of 1D AuNP chains. Several strategies have employed DNA molecules for AuNP assembly based on electrostatic interactions[22,23] or sequence-specific base pairing.[24] Polymers also have been used to organize AuNPs into 1D chains with some success.[7,25−27]Alternatively, 1D

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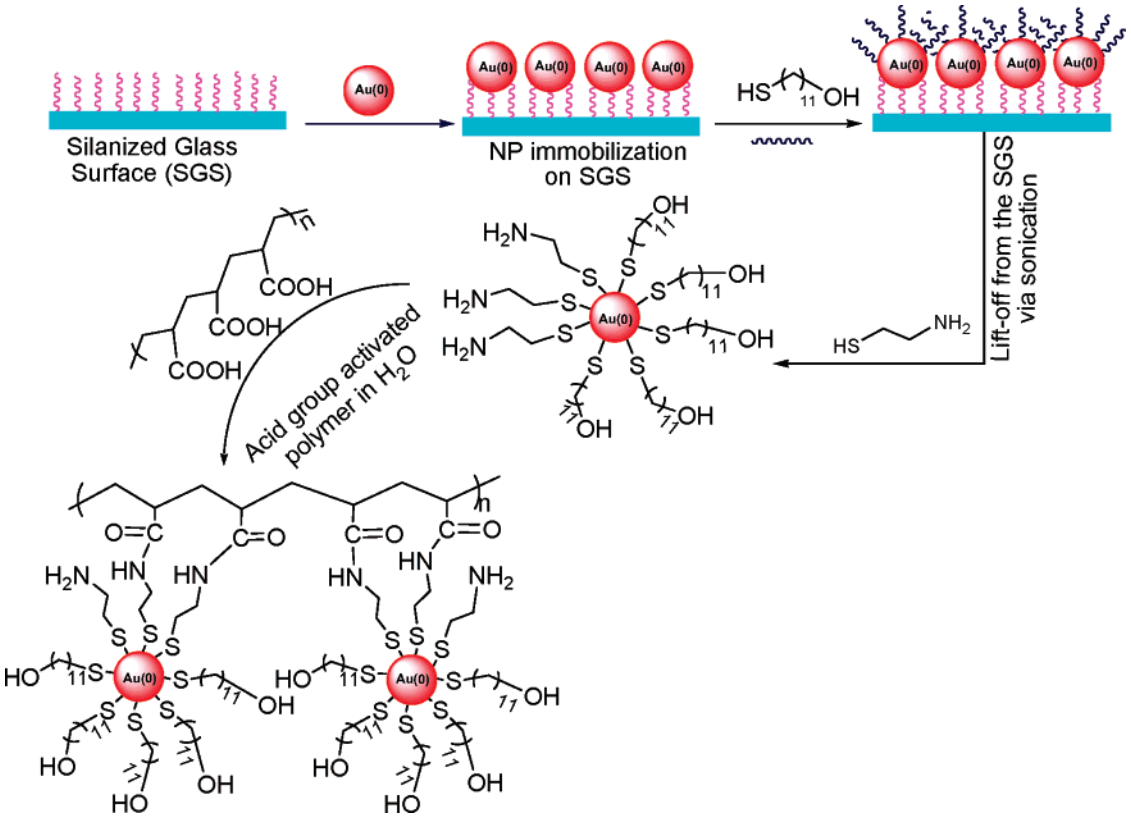
Scheme 1. Immobilization of Citrate-Stabilized AuNPs on a Silanized Glass Surface followed by Generation of Asymmetrically Functionalized AuNPs



AuNP chains have been prepared by controlling the composition of the ligand shell using a place exchange process[28] to produce divalent AuNPs that were assembled by interparticle covalent linkages. In general, these methods are limited in the size/type of particles that can be assembled and the ligands that can be used. In addition, approaches that involve preparation in organic solvents complicate use of the 1D AuNP chains in aqueous-based applications.

Our approach for assembling AuNPs into 1D chains using a polymer is carried out in aqueous solution and is demonstrated for a range of nanoparticle sizes. Different size AuNPs were synthesized using Frens's method.[29] The assembly process begins with solid-phase synthesis of asymmetrically functionalized AuNPs in water according to a previously described procedure as shown in Scheme 1.[16] Briefly, citrate-stabilized AuNPs were immobilized on an amine-terminated silanized glass surface (SGS) where amine groups likely displace citrate groups on the region of the nanoparticle surface that is in contact with the substrate. The AuNP-coated SGS was then immersed in an ethanolic solution of 11-mercapto-1-undecanol (MUOH). This step was carried out to displace the remaining citrate shell to create a self-assembled monolayer of MUOH molecules on the outer surface of the AuNPs. The MUOH-functionalized AuNPs were then removed from the SGS by sonication in an aqueous solution of 2-mercaptoethylamine (MEA). The MEA molecules bind to the region of the AuNP surface that had been associated with the amine-terminated SGS and not accessible to the MUOH molecules during the first functionalization step. The area of the AuNP surface associated with the amine groups on the SGS is small compared to the total surface area of the particle. Previous studies indicated that the MEA molecules bind to this localized bare region as the particle is released from the substrate, generating asymmetrically functionalized AuNPs.[16] The remainder of the AuNP surface is covered by MUOH ligands. To assemble the asymmetrically functionalized AuNPs, we exploited the amide-coupling reaction between the amine functional groups localized on the AuNPs' surfaces and pendent acid groups in poly(acrylic acid) (PAAc) as shown in Scheme 1. An aqueous solution of PAAc was prepared and then reacted with 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDAC) and 1-pentafluorophenol (PFP) to activate the acid groups. Finally, the asymmetrically functionalized AuNPs were added to an aqueous solution containing the polymer to form the 1D AuNP chains.

The LSPR properties of the AuNPs at different stages of the assembly process were monitored using UV−vis absorption spectroscopy (Figure 1a). Before the coupling reaction, the AuNPs were partially functionalized with MEA and produced a strong LSPR peak at 531 nm. The extinction measurements of MEA-functionalized AuNPs were performed on a glass substrate in air. After the reaction of MEA-functionalized particles with PAAc, two distinct absorption peaks were observed, one at 534 nm and the other at 614 nm. The red-shifted peak was likely due to a combination of a change of refractive index of the medium due to the presence of the polymer and also LSPR coupling between the AuNPs within the 1D chains.

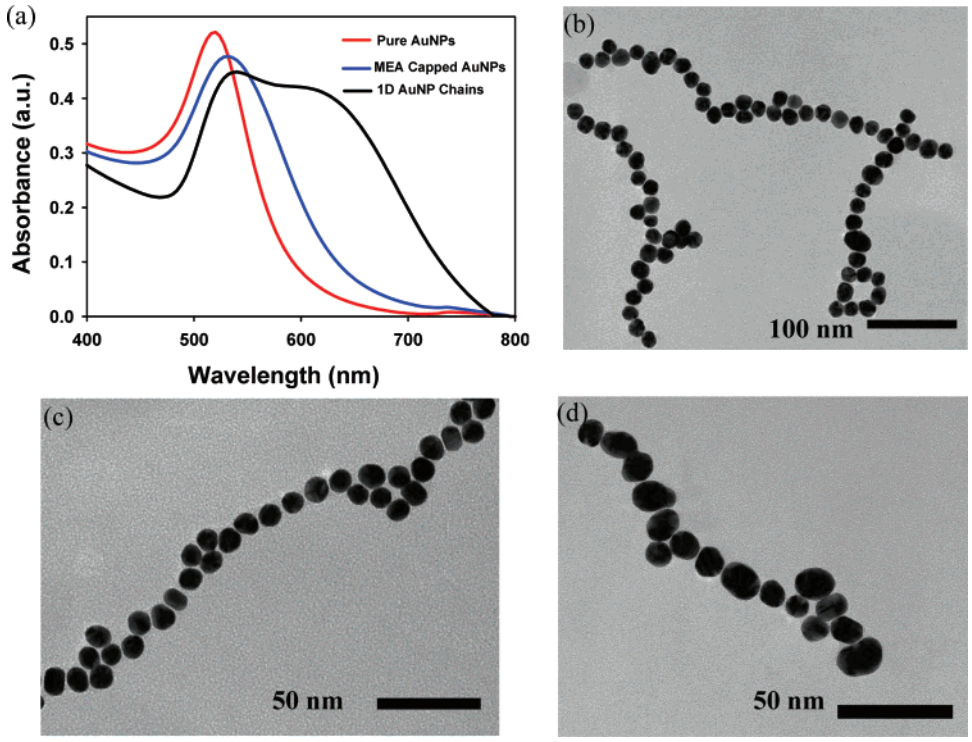


Figure 1. (a) UV−vis absorption spectra of the 16 nm diameter gold nanoparticles at different stages of the chain formation process. (b) TEM images of 1D chains formed by 16, (c) 10, and (d) 30 nm diameter AuNPs.

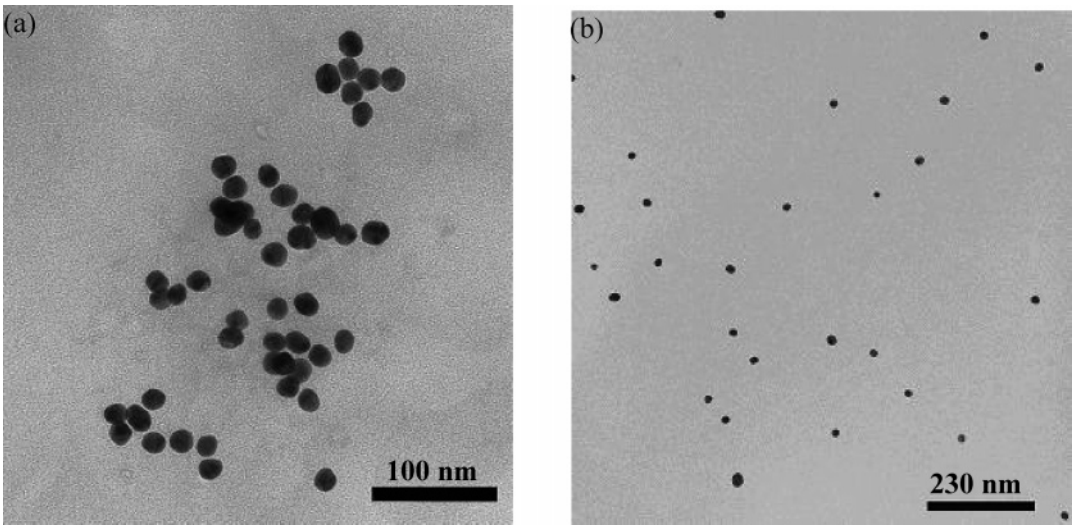


Figure 2. TEM images of the AuNPs after (a) ligand exchange with MHA and (b) mixing citrate-stabilized gold particles with PAAc.

Transmission electron microscopy (TEM) was used to analyze the asymmetrically functionalized AuNPs and the 1D AuNP chains. TEM analysis shows that the asymmetrically functionalized AuNPs prior to assembly with the polymer are dispersed and particle aggregation was not observed (data not shown). After assembly with the polymer, AuNP chains were formed with 14−18 nanoparticles per polymer chain (Figure 1b). In some cases, 1D AuNP chain networks were observed. These networks could be due to the attachment of two or more acid groups from different polymer chains to one AuNP or the entanglement of the polymer chains in solution or during TEM sample preparation. However, no three-dimensional (3D) aggregates were observed. A low percentage (~5%) of individual AuNPs also were observed along with the 1D AuNP chains. Under similar reaction conditions and identical molar ratio of reagents, we synthesized 1D chains of AuNPs with diameters of 10 and 30 nm (Figure 1, panels c and d, respectively). The formation of 1D AuNP chains is rationalized by our hypothesis that chain structures would be formed when partially amine (MEA) functionalized AuNPs were combined with EDAC and PFP activated PAAc to form covalent amide linkages between the amine groups on the AuNP surface and the carboxylic acid groups of PAAC as shown in Scheme 1. The asymmetry of the ligand shell (i.e., the localization of the MEA ligands) leads to a well-controlled 1D chain

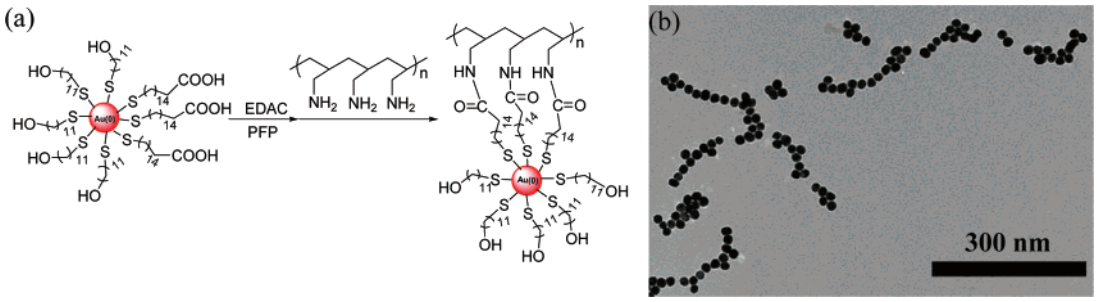


Figure 3. (a) Schematic diagram of covalent coupling of partially MHA functionalized AuNPs to amine groups along the backbone of PAAm. (b) TEM image of 1D chain formed by 16 nm diameter asymmetrically functionalized AuNPs.

assembly process with minimal network formation and no 3D aggregates.

Several control experiments provide evidence to support our hypothesis of the chain formation process. In the first experiment, free thiols in solution were exchanged with ligands attached to the assembled AuNPs. During the reaction, the 1D AuNP chains were incubated with 16-mercaptohexadecanoic acid (MHA). In the experimental procedure, 2 mL of 1 mM ethanolic MHA solution was added to 5 mL of a solution of 16 nm diameter AuNP chains, and the reaction mixture was stirred at room temperature for 48 h. During the place-exchange reaction, a mixed ligand shell on the gold nanoparticle surface composed of the initial capping ligand and the second ligand used in the exchange reaction should have been formed.[30,31] TEM analysis showed the presence of individual and broken AuNP chains (see Figure 2a) likely due to ligand exchange between the MHA in solution and the ligands on the AuNPs' surfaces. The high concentration of MHA molecules present in the solution could easily lead to replacement of the MEA molecules from the surface of the AuNPs, displacing AuNPs from the polymer.

According to our hypothesis, the amine-terminated, asymmetrically functionalized AuNPs are linked to the polymer through amide bonds with activated acid groups from pendent groups along the polymer backbone. The necessity of the terminal amine groups present on the asymmetrically functionalized AuNP shell is shown through a control experiment involving the addition of 1 mL of as prepared citrate-stabilized AuNPs (16 nm diameter) to 3 mL of pure PAAc solution (0.2 mg/mL). The TEM analysis showed the presence of dispersed, individual AuNPs (see Figure 2b) with no evidence for chain formation as expected. We also investigated the result of combining partially MEA-functionalized AuNPs with the PAAc in solution without EDAC and PFP. Without activating the acid groups on the PAAc, the AuNPs remain dispersed, and there is no evidence of chain formation from TEM analysis (see the Supporting Information). This provides indirect evidence of covalent attachment of the asymmetrically functionalized AuNPs to the polymer to form the 1D chains.

To demonstrate the versatility of the 1D chain assembly process and to provide further evidence for specific chemical attachment of the AuNPs to the polymer, the location of the acid group and the amine group were reversed by including an acid-terminated ligand on the AuNP and attaching the particles to the pendent amine groups along the backbone of poly(allylamine) (PAAm). For this experiment, 16 nm diameter AuNPs were asymmetrically functionalized with MHA in water shown in Figure 3a. The resulting nanoparticle solution was then reacted with EDAC in the presence of PFP to activate the acid groups on the nanoparticles' surfaces. An aqueous solution of PAAm was added to the nanoparticle solution. TEM analysis shows the formation of 1D AuNP chains with an average of 7−11 particles per chain, as shown in Figure 3b. The fewer number of particles in the chains in Figure 3b compared to the chains formed using PAAc shown in Figure 1b is probably due to the smaller molecular weight of the PAAm (~65 000 g/mol) compared to the PAAc (~450 000 g/mol). No 3D aggregates were observed. The results suggest that the activated acid groups on the partially acid-functionalized AuNPs nanoparticles formed amide bonds with the amine groups on the PAAm.

For many applications of metal nanoparticles, control of interparticle spacing in an assembly such as the 1D chain provides a means to tune the LSPR properties, including the localization of electromagnetic fields. For applications such as surface-enhanced Raman scattering (SERS), it has been observed that the interparticle spacing between two adjacent particles is very important.[32,33] When the particles are in close proximity, the local electromagnetic fields become focused producing a "hot spot" that provides a substantial portion of the enhancement in SERS. Because the importance of controlling the interparticle spacing, we investigated this in more detail. As shown in Figure 4d, the 1D AuNP chains exhibit regular interparticle spacing of 2.7 ± 0.4 nm (i.e., calculated from 100 different particles), which is close to twice the length of an extended MUOH ligand (3.02 nm). This spacing indicates that AuNPs form a close-packed assembly with the spacing between neighboring particles determined by the thickness of their MUOH ligand shells. The control of the interparticle spacing by changing the length of the ligands in the shells is shown in Figure 4a−c. When the longer ω-functionalized alkylthiol ligand 16-hydroxy-1-hexadecanethiol (HHDT) is used, the interparticle spacing increases to 3.3 ± 0.6 nm (Figure 4e). This spacing was greater compared to the interparticle spacing in the 1D chains synthesized in the presence of MUOH, 2.7 ± 0.4 nm (Figure 4d). The spacing between the two nanoparticles was further increased by using 1-mercaptoundecyl tetra(ethylene glycol) (MUTEG) as shown in Figure 4f. A comparative study was made for interparticle spacings within the 1D

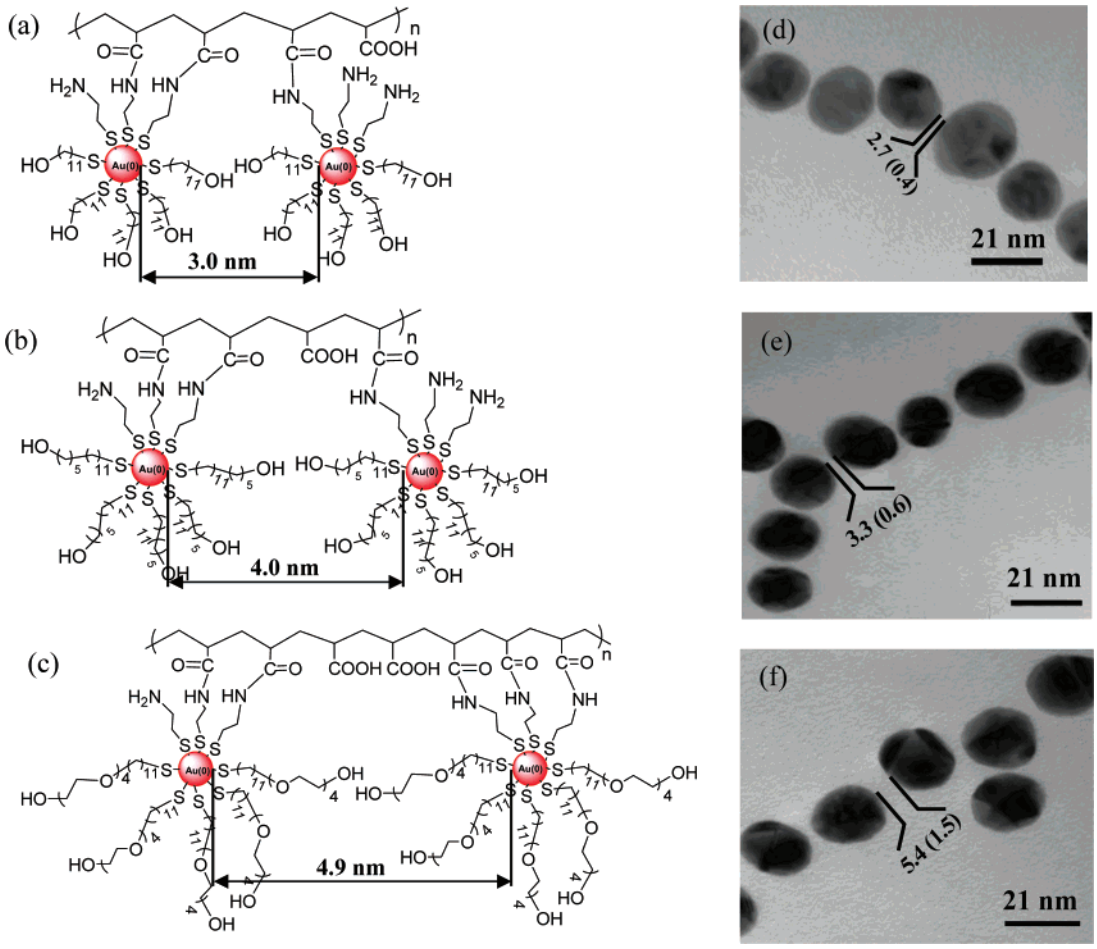


Figure 4. (a−c) Schematic representations of the formation of chains with different interparticle spacings based on using ligands with different lengths. (a) MUOH, (b) HHDT, and (c) MUTEG. TEM images of 1D AuNP chains in (d−f) show control of interparticle spacing using the ligands from panels a−c.

chains, and the results show that the separation between AuNPs increases as the length of the ligand increases and the distances measured in the TEM images compare very well with the calculated distances for these ligands (see Supporting Information, Table 1).

In conclusion, we have described a simple approach to organize asymmetrically functionalized AuNPs into 1D chains using polymers as templates. The asymmetric functionalization approach and the aqueous-based synthesis make the process versatile, environmentally friendly, and should facilitate applications in biotechnology. The assembly process produces a composite material that could provide dual advantages for structural (i.e., provided by the polymer)[34,35] and electronic or optical (i.e., provided by the nanoparticles) properties.[36,37] We have demonstrated the application of the chain formation methods for AuNPs with diameters of 10−30 nm, and the extension to a wider size range of particles is under investigation. Furthermore, we are able to control the interparticle spacing by varying the thiol used in the ligand shell. This control over particle spacing could be very useful in studying and tuning optical and electronic properties for many applications including device fabrication. This 1D chain formation should be broadly applicable for other types of nanoparticles with different sizes, shapes, or composition (e.g., semiconductor or magnetic).

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Supporting Information Available: Experimental details of gold nanoparticle synthesis, formation of 1D nanoparticle chain, additional TEM images, and a table. This materials is available free of charge via the Internet at http://pubs.acs.org.

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