

Silver Nanoparticles Assemblies Mediated by Functionalized Biomimetic Oligomers

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ABSTRACT:

The interaction between biopolymers and metal nanoparticles (AgNPs) is a key element in the development of biomimetic nanomaterials with applications in catalysis, delivery, and recognition. Here we report a facile method for the functionalization of AgNPs by *N*-substituted glycine oligomers, “peptoids.” Based on the established affinity between phenanthroline ligand and Ag(0), we synthesized a peptoid bearing 1,10-phenanthroline at the *N*-terminus (PHP). Treatment of AgNPs that were pre-stabilized by citrate ions, with PHP, leads to the formation of aggregates as suggested by UV–vis spectroscopy. Transmission electron microscopy (TEM) revealed that the replacement of citrate ions by PHP yields spherical assemblies of AgNPs. These peptoids/AgNPs hybrids, as well as the ability of functional biomimetic oligomers to mediate the assembly of metal nanoparticles, hold potential for applications in sensor materials, biology,

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Keywords: peptoid; nanoparticle; silver; assembly; aggregation

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INTRODUCTION

The organization or self-assembly of nanoparticles (NPs) in multiple dimensions harness their nanoscale attributes and provides unique electrical and optical properties.¹ Ensembles containing both metal NPs and organic or bioorganic molecules are of special interest because they display the properties of both components, leading to a variety of applications in biology, medicine, and sensing.^{2–6} Such assemblies enable interparticle interactions and structures that create interfacial or interparticle binding sites for molecular interaction or recognition, which is the basis of chemical sensing. For example, the sorption of volatile organic compounds (VOCs) on NPs assemblies leads to a change in electron hopping or tunneling properties depending upon particle size and interparticle distance. Similarly, NPs assemblies are used as probes for the separation and detection of DNAs, proteins, and VOCs via interparticle amplification of optical and surface-enhanced Raman scattering (SERS) signals.

Metal-based functional NPs are typically synthesized using stabilizers containing functional groups that can interact with the nanoparticle surface, e.g., thiols,⁷ amines,^{8,9} carboxylates,¹⁰ or phosphines.¹¹ The synthesis involves either the direct functionalization method, in which the functional group also acts as a stabilizing agent,¹² or the post-function-

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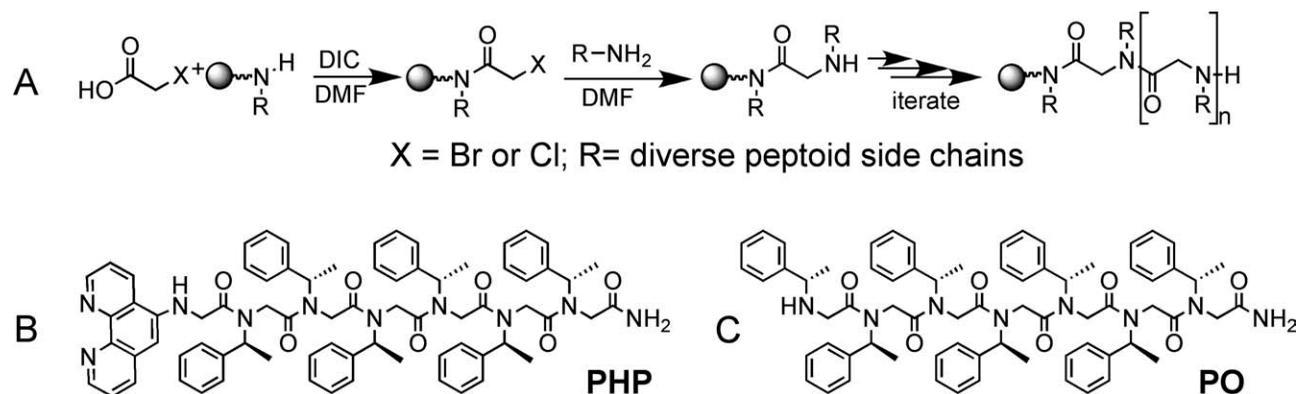
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SCHEME 1 Solid-phase “sub-monomer” peptoid synthesis (A) and the peptoids **PHP** (B) and **PO**(C).

alization method, in which the metal NPs are stabilized by a labile ligand that is easily replaced by the functional group.⁷ The pendant ligands, also known as capping agents, may enable the NPs aggregation into ordered assemblies with unique properties.^{1–6} A variety of techniques, such as layer-by-layer stepwise assembly,¹³ polymer- or dendrimer-mediated organization,^{14,15} and DNA-mediated assemblies^{16,17} have been employed for the controlled aggregation of metal NPs. In addition, peptide oligomers have been used to functionalize metal nanoparticles^{18–20} and mediate their assembly into aggregates,²¹ three-dimensional architectures,²² nanorods,²³ nanoreactors,²⁴ and optically responsive materials.²⁵ Most of these examples, however, report the aggregation of gold nanoparticles, while the synthesis of functional silver aggregates has not been explored broadly,^{20,26} possibly because the aggregation of silver nanoparticles is more difficult to control.²⁷ Therefore, it is desirable to develop new strategies for the stabilization of silver nanoparticle assemblies. In addition, the use of polymers or dendrimers for the construction of NPs assemblies is synthetically challenging and it is limited by the polymers/dendrimers functionalization as well as by their compatibility with biotic conditions such as water solubility and low toxicity. The use of peptides as capping agents is synthetically more effective; however, applications are still inadequate, mainly because peptides exhibit limited stability with regard to variation in pH, temperature, and the presence of organic reagents. Consequently, there is a need for biomimetic scaffolds that can be easily generated, functionalized, and mediate the aggregation of metal NPs, including silver NPs, for the construction of organic–inorganic hybrid assemblies, which are compatible with a wide range of temperatures, pH, chemical reagents, and more.

N-substituted glycine oligomers or “peptoids,” are artificial mimics of peptides^{28,29} that can be synthesized efficiently by the solid-phase “sub-monomer” protocol³⁰ (Scheme 1A),

a method that usually requires no protecting groups, involves a minimal number of purification steps, allows ambient temperatures (typically 25°C) and short reaction times, and can be automated. The “sub-monomer” method, which employs primary amine synthons, enables the incorporation of innumerable functional groups at specified *N*-positions along the peptoid backbone and facilitates the generation of peptoid oligomers possessing a wide range of chemical and structural diversity.³¹ For example, carboxyl and amine groups, which are known for their affinity to gold and silver nanoparticles, have been incorporated as side chains within a variety of peptoid sequences.^{32,33} Some of these peptoid sequences are soluble in water, an important property for biological applications of metal nanoparticles.³⁴ In addition, peptoid oligomers are thermally stable and compatible with abiotic solvents.³⁵

Recently, we have described the introduction of bi-dentate and tri-dentate metal-binding ligands as pendant groups in peptoid sequences.³⁶ In this context, the adsorption of the bi-dentate ligand 1,10-phenanthroline on metallic surfaces, including its interaction with metal NPs, has been explored previously by both theoretical and experimental studies.^{37,38} Specifically, gold and silver NPs coated by 1,10-phenanthroline ligand or 1,10-phenanthroline-terminated ruthenium(II) complexes as capping agents were synthesized, and the interactions between the metal NPs and these capping agents were investigated.^{39,40} These studies revealed that: (i) using the direct functionalization method, 1,10-phenanthroline-terminated ruthenium(II) complexes (Phen-Ru) can stabilize Ag(0) NPs of sizes between 1 and 8 nm depending on the Ag(I):Phen-Ru ratio (smaller particles were formed in smaller ratios) and (ii) the stabilization of Ag(0) NPs by either the direct or the post-functionalization methods are highly pH dependent; distinct NPs were only obtained when the pH of the solution was maintained below the pK_a of

phenanthroline, 4,9, with partial aggregation taking place after a few hours (the aggregates were not characterized). Herein we present our preliminary results, which demonstrate that capping aqueous silver NPs (AgNPs) with peptoid oligomers bearing 1,10-phenanthroline at the *N*-terminus (**PHP**, Scheme 1B) leads to the aggregation of the particles into spherical assemblies, as shown by UV-vis spectroscopy and transmission electron microscopy (TEM). The ability of functional biomimetic oligomers to mediate the assembly of metal NPs is the first step toward the generation of unique materials with properties deriving from both components of the organic-inorganic ensemble.

MATERIALS AND METHODS

Synthesis and Purification of the Peptoid Oligomers PO and PHP

Solid-phase synthesis of peptoid oligomers was performed in fritted syringes on Rink amide resin using a variation of a previously reported peptoid sub-monomer protocol.³⁰ In a typical oligomer synthesis, 100 mg of resin with a loading level of 0.69 mmol g⁻¹ was swollen in 4 mL of dichloromethane (DCM) for 30 min. Following swelling, the Fmoc protecting group was removed by treatment with 1.5 mL of 20% piperidine in dimethylformamide (DMF) for 20 min. After de-protection and after each subsequent synthetic step, the resin was washed three times with 2 mL of DMF, 1 min per wash. Peptoid synthesis was carried out with alternating bromoacylation and amine displacement steps. For each bromoacylation step, 20 equiv bromoacetic acid (1.2 M in DMF, 8.5 mL g⁻¹ resin) and 24 equiv *N,N'*-diisopropylcarbodiimide (neat, 2 mL g⁻¹ resin) were added to the resin, and the mixture was agitated for 20 min. After washing, 20 eq. of the required amine (1.0 M in DMF) were added to the resin and agitated for 20 min. For the synthesis of **PHP**, this protocol was modified as follows: the last amine displacement with 1,10-Phenanthroline-5-amine (20 eq., 0.33 M in DMF, 10 mL g⁻¹ resin) was performed for 16 h. When the desired sequence was achieved, the peptoid products were cleaved from the resin by treatment with 95% trifluoroacetic acid (TFA) in water (40 mL g⁻¹ resin) for 15 min. After filtration, the cleavage mixture was concentrated by rotary evaporation under reduced pressure for large volumes or under a stream of nitrogen gas for volumes less than 1 mL. Cleaved samples were then re-suspended in 50% acetonitrile in water and lyophilized to powders. **PO** and **PHP** were purified to >95% purity by preparative High performance liquid chromatography (HPLC) using a C18 column. Products were detected by UV absorbance at 230 nm during a linear gradient conducted from 5 to 95% solvent B (0.1% TFA in HPLC grade acetonitrile) over solvent A (0.1% TFA in HPLC grade water) in 50 min with a flow rate of 2.5 mL min⁻¹. Analytical data for **PHP**: HPLC: *t*_R = 8.2 min; linear gradient: 5–95% solvent A over solvent B in 10 min with a flow rate of 0.7 mL min⁻¹. MS (ESI): *m/z* = 1219.5 calcd for C₇₄H₇₈N₁₀O₇ [M+H]⁺; found: 1219.5 (Agilent 1100 Series LC/MSD Trap XCT).

Synthesis of AgNPs Assemblies

Citrate-stabilized AgNPs were synthesized according to previously published procedures.^{41,42} Cl-Phen-capped AgNPs assemblies were prepared by the post-functionalization method: citrate-stabilized AgNPs solution (1 mL) was combined with 1 mL solution of 5-chloro-1,10-phenanthroline (1:1 water:acetonitrile, 1 mM) and vigorously stirred for 10 min, resulting in a light-pink colloidal solution. The pH of both solutions was adjusted to values ranging from 3.0 to 7.0, prior to mixing, by addition of hydrochloric acid (1 mM) and sodium hydroxide (10 mM). **PHP**-capped AgNPs assemblies were prepared by the post-functionalization method: citrate-stabilized AgNPs solution (1 mL, pH = 3.5) was added to a 1 mL solution of **PHP** (1:1 water:acetonitrile, 1, 0.5, or 0.25 mM, pH = 3.5) and the reaction was vigorously stirred for 10 min, resulting in a light-red colloidal solution.

UV-Vis Spectroscopy and Transmission Electron Microscopy

A Lambda 950 double beam double monochromator, and ratio recording UV/VIS/NIR spectrophotometer with a resolution ≤0.05 nm was used for UV-vis measurements. Samples (3 mL solutions placed in a quartz cuvette) were consisted of citrate-stabilized AgNPs, **PHP**, Cl-Phen-capped AgNPs, or **PHP**-capped AgNPs solutions (0.48 mL) diluted in 2.52 mL of water. Transmission electron microscopy (TEM) was performed using a JEOL 1230 electron microscope operating at 200 kV. For TEM analysis, samples of Cl-Phen- and **PHP**-capped AgNPs solutions were freshly prepared, centrifuged at 2000 rpm for 90 min prior to liquid decantation and the solid mass was filtered, washed with water, dried, and re-dispersed in a solution of 1:1 water:acetonitrile.

RESULTS AND DISCUSSION

Synthesis of PHP Oligomer

Peptoid heptamer **PHP**, bearing six (S)-(–)-1-phenylethyl side chains and 1,10-phenanthroline at the *N*-terminus, was synthesized on Rink amide resin using a variation of a previously reported peptoid submonomer protocol (Schemes 1A and 1B).³⁰ Typically, *N*-alkyl-substituted glycine units are generated by the iteration of successive short bromoacylation and amine displacement steps (>20 min). Because of the deactivated character of 5-amine-1,10 phenanthroline⁴³ and its low solubility in DMF, a longer reaction time and a lower concentration were applied in the last step of the synthesis. The product was cleaved from the resin with aqueous trifluoroacetic acid, analyzed by analytical high-performance liquid chromatography (HPLC), purified by preparative HPLC, and its sequence, as well as the incorporation of the phenanthroline ligand, was confirmed by electrospray mass spectrometry. In general, both the pyridine-like nitrogen and the aniline-like nitrogen have a nucleophilic character, therefore the possibility exists that they will both attack the elec-

trophilic peptoid and a mixture of products will be generated. However, it is well known that substitution reactions of that type (bimolecular nucleophilic substitution) are kinetically favored with small and unhindered nucleophiles. In our case, the aniline-like nitrogen should be a better nucleophile than the aromatic ones, which are much more sterically hindered, and therefore we believe that the nucleophilic attack occurs by the primary amine to produce **PHP** solely rather than a mixture of products.

Synthesis of AgNPs in Different pH Conditions

The synthesis of gold and silver nanoparticles coated by 1,10-phenanthroline ligand or 1,10-phenanthroline-terminated ruthenium(II) complexes was studied extensively employing direct functionalization methods.³⁹ Recently, a post-functionalization approach was developed, in which increased homogeneity and stability of the phenanthroline-stabilized gold nanoparticles in solution was obtained.⁴⁰ Therefore, we decided to use the post-functionalization method for the capping and stabilization of AgNPs with **PHP**. The ability of 1,10-phenanthroline-terminated ruthenium(II) complexes to post-stabilize gold nanoparticles as described previously, was, however, highly pH dependent. Gold nanoparticles were only stable in solutions with pH below 4.9, the pKa of phenanthroline; above this pH, rapid aggregation occurred leading to a dark precipitate.⁴⁰ These studies suggested that electrostatic repulsion induced by the protonated phenanthroline ligands is essential for efficient stabilization of the NPs in water, hence, the protonated phenanthroline ligands electrostatically stabilize the metal NPs. On the basis of these observations, we sought to evaluate optimal pH conditions for the formation of **PHP**-capped AgNPs. The compound 5-chloro-1,10-phenanthroline (Cl-Phen) was used as a model ligand for the post-functionalization of citrate-stabilized AgNPs in a pH range of 3–7. Citrate-stabilized AgNPs, which are known precursors for post-functionalization processes,⁴⁴ were prepared according to a previously reported procedure.⁴¹ The yellow aqueous solution of citrate-stabilized AgNPs (0.25 mM, typically 1 mL) and the colorless 1:1 water:acetonitrile solution (due to the low solubility of both phenanthroline and **PHP** in water, these compounds were first dissolved in acetonitrile and then an equivalent amount of water was added) of Cl-Phen (1 mM, 1 mL) were adjusted to different pH values by treatment with various amounts of hydrochloric acid and sodium hydroxide, prior to mixing for 10 min at room temperature. Upon addition of citrate-stabilized AgNPs solution to the Cl-Phen solution at various pH conditions, a behavior similar to the previously reported one was observed. At pH < 4.9, an immediate color change, from yellow

to light pink, was detected. Above this pH, the color of the solution changed from yellow to blue, followed by a precipitation of dark solid particles that resulted in a colorless solution. Accordingly the synthesis of **PHP**-capped AgNPs was performed at pH < 4.9 employing a similar procedure as described above. The color of the solution changed from yellow to light red.

Aggregation of AgNPs by Post Functionalization with Cl-Phen and PHP

The optical properties of metal nanoparticles stem from their surface plasmon resonance, a phenomenon that is attributed to the collective oscillations of conduction electrons within the particles.^{2,45} This resonance frequency, the surface plasmon absorption band, lies in the visible part of the electromagnetic spectrum, giving rise to intense colors from solutions of colloidal metal particles. AgNPs exhibit high efficiency of plasmon excitation and possess a particle size-dependent surface plasmon resonance between 390 and 420 nm.^{46,47} The surface plasmon absorption band, and consequently the color of a metal nanoparticle solution, is dependent on several parameters, among which are the size and shape of the particle, the type of metal, the polarity of the solution and the distance between particles.⁴⁶ For example, small particles will have a plasmon band at a smaller wavelength than larger particles or aggregates.⁴⁵ Herein, mixtures of AgNPs and Cl-Phen solutions prepared in different pH conditions, were subject to UV-vis measurements and characterized by their plasmon absorption spectra.

Citrate-stabilized AgNPs exhibit a characteristic plasmon band near $\lambda = 390$ nm in water at different pH conditions. The stability of the Cl-Phen-capped AgNPs, however, is clearly pH-dependent, as different absorption spectra were obtained at different pH values (see Figure 1). In all cases, new plasmon bands ranging from 410 to 800 nm were formed, accompanied by a decrease of the band near 390 nm. At pH = 3.5, a single band near $\lambda = 410$ nm was observed. The shift of the surface plasmon band in this case may be attributed to the interactions between AgNPs and Cl-Phen.⁴⁰ At pH = 3.9 and 4.9 a second band was observed near $\lambda = 490$ and 520 nm respectively, indicating the formation of bigger particles or aggregates, a process that is associated with dipole coupling between the plasmons of neighboring particles.⁴⁷ Above pH = 4.9 rapid aggregation occurred as indicated by a broad absorption band near $\lambda = 600$ nm. At pH = 3.0 there is some stabilization of NPs aggregates with a plasmon band near $\lambda = 410$ nm, but its low intensity and the broad absorbance band near $\lambda = 800$ nm suggest that a different type of aggregates or very large ones are also formed

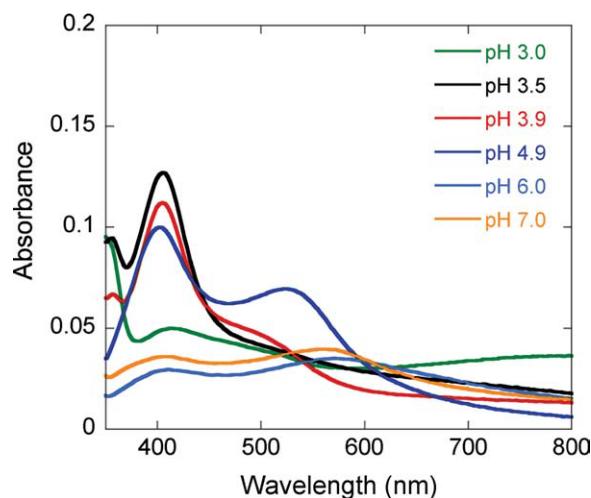


FIGURE 1 Absorption spectra of Cl-Phen-capped AgNPs at different pH conditions. AgNPs (1 mL) were post-stabilized with 5-chloro-1,10-phenanthroline (1 mM in 1 mL 1:1 water:acetonitrile solution).

and are present in the solution. As concluded by the previous studies,⁴⁰ gold NPs are not stabilized in water when interacted only with non-protonated phenanthroline ligand because the NPs need to be surrounded by ions in order to facilitate their dispersion in aqueous solution. The same explanation is valid in our case, where at $\text{pH} > 4.9$, AgNPs are destabilized because they interact solely with the non-ionic phenanthroline ligands Cl-Phen. At $\text{pH} < 4.9$, however, the aggregation process is limited; it decreases as the pH gets lower, and eventually diminishes at $\text{pH} = 3.5$. A suggested explanation to this aggregation process may involve the electrostatic interactions between the phenanthroline ligands, which are protonated at $\text{pH} < 4.9$, and both Cl-Phen and the citrate ions.⁴⁰ The formation of ion pairs between the Cl-Phen cations and the citrate anions should reduce the capability of the citrate to stabilize the AgNPs, leading to the AgNPs aggregation. This aggregation is limited, however, by the protonated Cl-Phen ligands that interact with the AgNPs and cap them, resulting in the termination of the aggregation process.

Based on the observation that a single plasmon band was obtained only at $\text{pH} = 3.5$, UV-vis measurements of citrate-stabilized AgNPs, PHP and PHP-capped AgNPs were performed at $\text{pH} = 3.5$ (see Figure 2). PHP exhibits absorption bands near $\lambda = 287$ and 343 nm in water:acetonitrile solution. Upon mixing of PHP (1 mL, 1:1 water:acetonitrile solution, 1 mM) with citrate-stabilized AgNPs (1 mL), a plasmon band near $\lambda = 440$ was produced (Figure 2, spectrum 3), suggesting that new assemblies, different from the aggregates

that were generated by the interaction of the AgNPs with Cl-Phen, have been formed. This absorbance spectrum, however, included a residual band at $\lambda = 343$ nm, which is attributed to the absorption of PHP. Therefore we decided to reduce the concentration of PHP. Mixing 0.5 mM solution (1 mL, 1:1 water:acetonitrile) of PHP with citrate-stabilized AgNPs afforded a slightly shifted plasmon band near $\lambda = 437$ nm. This spectrum, however, still contained a small residue of the band at $\lambda = 343$. The absorption band at $\lambda = 343$ diminished with the use of 0.25 mM solution, which resulted in a plasmon band near $\lambda = 445$ nm. As mentioned above, the strong shift in the UV-vis spectra from $\lambda = 390$ nm (a plasmon band associated with citrate-stabilized AgNPs) to $\lambda = 440$ nm (associated with PHP-capped AgNPs) indicates the formation of aggregates or nanoparticle assemblies. The minor differences in the plasmon bands, which are caused upon variations in the concentration of PHP may be attributed to small differences in size and/or shape of the assemblies.^{39,40}

PHP Mediates the Formation of Spherical AgNP Assemblies

Transmission electron microscope (TEM) images of citrate-stabilized AgNPs at $\text{pH} = 3.5$ showed spherical particles with average diameter of ~ 10 nm (Figure 3A). TEM images of the Cl-Phen-capped AgNPs revealed that replacement of citrate by Cl-Phen leads to aggregation of the nanoparticles, as suggested by UV-vis measurements. These aggregates, however, are not uniform in size and shape (Figure 3B). In contrast, PHP-capped AgNPs aggregate to form spherical assemblies, with sizes of about 70 nm in diameter, as shown by

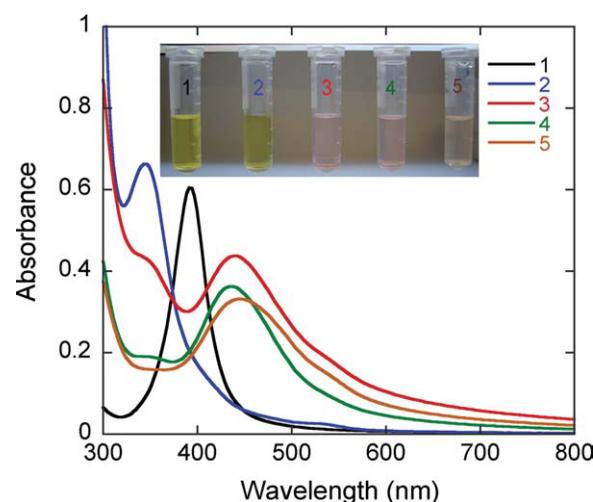


FIGURE 2 Absorption spectra of PHP-capped AgNPs at $\text{pH} = 3.5$ (1) Citrate stabilized AgNPs (2); PHP, 160 μM (3–5) AgNPs (1 mL) post-stabilized with PHP (1 mL), 1, 0.5, and 0.25 mM respectively, in 1:1 water:acetonitrile solution.

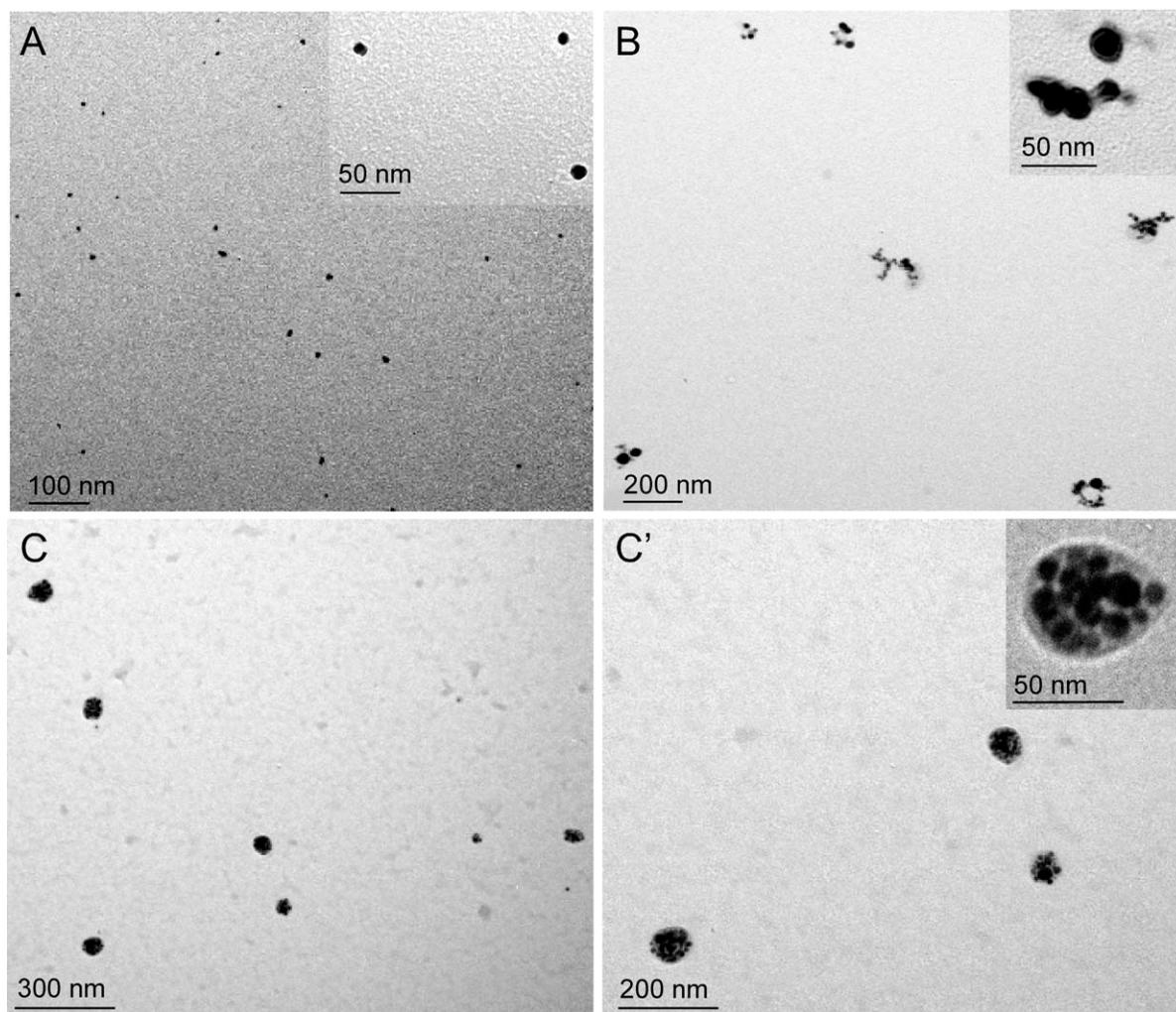


FIGURE 3 TEM images of (A) citrate-stabilized AgNPs; (B) aggregates of Cl-Phen-capped AgNPs; (C) and (C') discrete spherical assemblies of PHP-capped AgNPs.

TEM images (Figures 3C and 3C'). Moreover, the particles in Figure 3C' appear to be encapsulated in a defined medium, which is not present in Figure 3B and therefore can be attributed to the hydrophobic organic peptoid oligomers interacting with each other. These hydrophilic interactions seem to mediate the arrangement of the NPs into spherical assemblies and limit their size. The clear differences between Figures 3B and 3C' support the different UV-vis spectra obtained for these assemblies at pH = 3.5 (Figure 1, black line and Figure 2, red line). Based on the UV-vis spectra presented in Figure 1, it was suggested that interactions between the Cl-Phen ligands and the citrate-stabilized AgNPs result in size limited aggregates (see above). This process is schematically represented in Figure 4A. The same aggregation process may occur when PHP oligomers are interacting with both the citrate ions and the AgNPs, but in this case, the additional oligo-

meric chains serve as templates that mediate the aggregation of the AgNPs into discrete nano assemblies (Figure 4B). Therefore, capping of AgNPs with peptoid oligomers not only brings about the formation of aggregates, but also has a role in controlling their morphology. The capability of this peptoid to template the formation of NPs aggregates resembles the assembly of NPs mediated by polypeptides.^{48,49}

Establishing the Role of PHP in Mediating the Aggregation of AgNPs into Spherical Assemblies

In order to examine the role of the phenanthroline ligand in the functionalization of the AgNPs, we synthesized a peptoid heptamer, which does not contain a phenanthroline ligand but rather a phenylethyl-amino group at the *N*-terminus (PO, Scheme 1C). We wished to investigate the ability of PO to stabilize AgNPs or AgNPs aggregates and mediate the for-

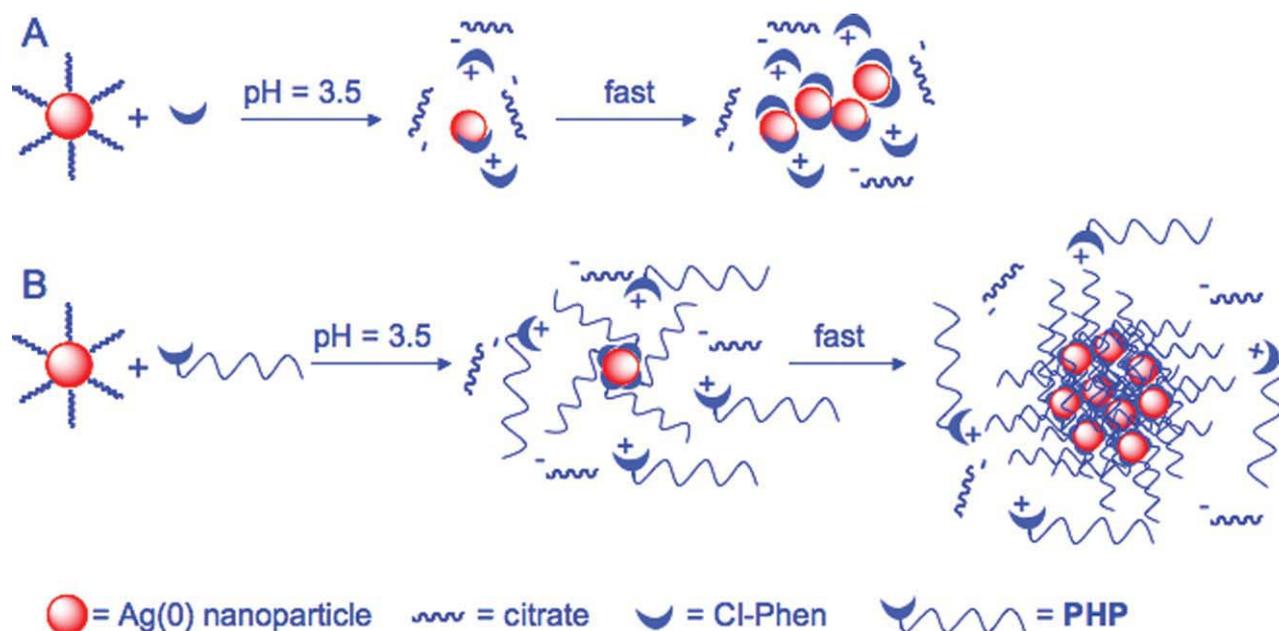


FIGURE 4 Functionalization of Ag(0) NPs by Cl-Phen (A) or PHP (B) and their random aggregation (A) or controlled aggregation into spherical assemblies (B).

mation of assemblies as in the case of **PHP**. First, we examined **PO** by itself at the same conditions we investigated **PHP**. Mixing 1 mL of citrate-stabilized AgNPs with 1 mL solution of **PO** (0.25 mM in 1:1 water:acetonitrile) at pH = 3.5, resulted in a rapid aggregation followed by the precipitation of a gray solid, and the yellow solution became colorless. Consequently, no absorbance band was recorded in the UV-vis spectrum of this solution (Supporting Information Figure S5). These results indicate that **PO** is unable to replace the citrate ion and stabilize AgNPs assemblies in these conditions; therefore the incorporation of the phenanthroline ligand is necessary for the functionalization of the AgNPs. Moreover, the secondary amine at the *N*-terminus of **PO** is not only unable to post-functionalize AgNPs in these conditions, but it actually destabilizes the NPs by forming electrostatic interactions with the acidic citrate ligands, which are capping the NPs. Thus, **PO** molecules reduce the ability of the citrate anions to stabilize the NPs against agglomeration, and therefore enable the rapid aggregation and precipitation. We then decided to investigate the interactions of **PO** with AgNPs in the presence of Cl-Phen. Notably, the addition of citrate-stabilized AgNPs solution (0.16 mL) to a 1:1 mixture of Cl-Phen and **PO** solution (0.32 mL, 1:1 water:acetonitrile) at pH = 3.5 did not produce peptoid/AgNPs hybrid assemblies; instead, large Ag(0) colloids were generated (Supporting Information Figure S6). Based on our above observations regarding the interactions of each ligand, either **PO** or Cl-

Phen, with AgNPs, we can suggest that in this case, initiation of the aggregation process, which is due to the destabilization of the AgNPs by **PO** molecules, is followed by capping of the aggregates with Cl-Phen ligands leading to large colloids dispersed in the solution. The fact that neither **PO**, Cl-Phen nor a mixture of both could mediate the formation of spherical AgNPs assemblies as **PHP** does, demonstrates that attachment of the phenanthroline ligand to the peptoid scaffold is required for the formation of peptoid/AgNPs hybrid assemblies and establishes the significant role of **PHP** in this process.

Stability of PHP-Capped AgNPs

In general, the **PHP**-capped AgNP assemblies are not stable in solution, and precipitate as a light-orange solid after a few days. In order to evaluate the stability of the solid AgNPs assemblies, 1 mL solutions of **PHP**-capped AgNPs were centrifuged at 2000 rpm for 90 min. The liquid was decanted and the solid mass was filtered, washed with water, dried and re-dispersed in a solution of 1:1 water:acetonitrile. Characterization of a solution sample by TEM, before and after the centrifugation, revealed no change in either the size or the shape of the AgNPs assemblies. The method is reproducible, and the solid AgNPs assemblies remain stable for weeks when stored under ambient conditions.

CONCLUSIONS

This work describes the assembly of AgNPs by peptoid oligomers to form peptoids/AgNPs hybrids. We demonstrate that the capping of AgNPs with peptoid oligomers enables their specific aggregation into well-defined spherical shaped assemblies, accompanied by a distinct color change of the NPs solution. Though a variety of biopolymers and peptides have been found to stabilize gold and silver NPs, we believe that the scope of properties and applications, such as chemical and biological sensing as well as selective catalysis, can be enlarged by the design of biomimetic oligomers that are able to functionalize metal NPs. Peptoids, which can be easily generated and are compatible with various temperatures, pH conditions and abiotic solvents, represent a unique opportunity for functionalizing and assembly of metal NPs toward applications in biology, catalysis and materials science. The study presented here is the first observation that synthetic biomimetic oligomers can be employed as a template for the assembly of metal NPs. Further efforts will target numerous sequences varied in length and composition for the stabilization of functional metal NPs and for the controlled aggregation of assemblies with new properties such as water solubility, chirality and more.

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