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A “Macrocyclic Effect” on the Formation of Capped Silver Nanoparticles in DMF

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The formation of silver nanoparticles in the presence of various macrocyclic thiol compounds in *N,N'*-dimethylformamide (DMF) solution was investigated in situ through visible spectrophotometric and photon correlation spectroscopic measurements. While temperature, solvent nature, and the concentration of thiol compounds are important parameters in the process of metal cluster and particle generation, the chemical structure of the thiol capping molecules also plays a crucial role at determining the average particle size. In this work, we report, for the first time, the existence of a “macrocyclic effect” on silver particle formation by using two types of thiol macrocyclic compounds, thiolated β -cyclodextrins (β -CD) and thiolated cavitands. Perthiolated β -CD was found to be more efficient as a capping ligand than monothiolated β -CD. Similarly, a tetrathiolcavitand derivative was also more efficient than a simple monothiol model compound. The macrocyclic thiol ligands led to more stable and smaller particles, a finding that may prove useful in future wet schemes for the preparation of metal nanoparticles functionalized with organic monolayers.

Since the seminal report by Brust and co-workers,¹ metal nanoparticles stabilized by thiol molecules have become an exciting and very active area of interdisciplinary research, including topics such as self-assembly of nanocomposites,² catalysis,³ and chemical⁴ and biological sensing.⁵ Among these, the functionalization of nanoparticle surfaces with molecules capable of engaging in well-defined host–guest interactions is receiving considerable attention.⁶ Our group has focused on the modification of gold,⁷ platinum,⁸ and palladium^{8,9} nanoparticles with thiolated cyclodextrins (CDs) with the primary goal of expressing their well-documented host properties on the nanoparticle surfaces. In this type of research work, the preparation of metal nanoparticles with desired size and

surface function is of crucial importance. While temperature and the nature of solvent and reducing agent have a strong influence on particle formation, the choice of thiol capping molecule is also very important in order to obtain monolayer-protected metal nanoparticles with the desired particle sizes.¹⁰ However, there is a paucity of hard data on how the structures of thiol molecules influence the process of particle formation. This is a fundamental issue that needs to be addressed as we improve our understanding of the kinetic and thermodynamic factors that control the generation of metal nanoparticles functionalized with various types of capping ligands.

The term *macrocyclic effect* refers to the increased thermodynamic stability of a complex formed between a metal ion and a multidentate macrocyclic ligand as compared to the complex between the same ion and the corresponding open-chain ligand(s). The macrocyclic effect has an entropic origin; that is, it results from the spatial preorganization of donor groups around the central metal ion.¹¹ The conceptual similarities between the coordination of metal ions by ligands and the capping of metal particles by organic molecules led us to investigate the effects that a macrocyclic arrangement of thiol groups may have on the preparation of capped metal nanoparticles. The results of these experiments may provide additional insight on how the structures of thiol molecules and other capping ligands influence the process of particle formation.

The structures of the thiol capping ligands¹² selected for this work are shown in Chart 1. *N,N'*-Dimethylformamide (DMF) was used as both the solvent and the reducing agent in the preparation of silver nanoparticles by reduction of silver nitrate.¹³ There are several key considerations on the selection of DMF and silver nanoparticles as the key components of the system investigated

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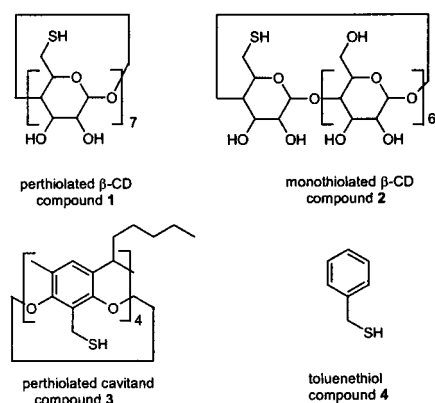
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Chart 1



here. First, the kinetics of reduction of silver ion and subsequent particle growth can be tuned simply by setting the proper reaction temperature, since DMF is a weak reducing agent and the reduction process is extremely slow at room temperature. Second, compared to common metal particle preparation methods, this system requires fewer components because there is no need to add a reducing agent. Therefore, the overall kinetics of particle formation is not affected by the rate of addition of reducing agent. DMF is also a good solvent for the thiol compounds used in this study. Finally, one can easily monitor silver particle formation in situ by recording their typical surface plasmon band (SP band),^{13,14} which is very sensitive to surface modification and particle size.

Cyclodextrins are cyclic oligomers with various numbers of glucopyranose units depending on their structures.¹⁵ They have been extensively studied as host molecules in supramolecular chemistry.¹⁶ We have utilized perthiolated α -cyclodextrin (α -CD),^{7b,d} perthiolated β -cyclodextrin (β -CD),^{7a,b,d,8,9} and perthiolated γ -cyclodextrin (γ -CD)^{7b,c} to modify metal nanoparticles in our previous work. Here, we decided to use perthiolated β -CD (compound 1) as an example of a typical macrocyclic capping ligand, because it contains a rim of seven thiol groups arranged to permit their simultaneous interaction with a metal surface. In contrast, 2 was selected because it has a very similar structure, but only one thiol group per ligand molecule. Ligand 2 is not a macrocyclic thiol in the sense that its thiol binding properties are necessarily those of a monodentate ligand. In a typical experiment, 3 mL of DMF in a cuvette containing either thiol compound was heated to 60 °C in the temperature-controlled cell holder of the UV-vis spectrophotometer. After adding Ag^+ (20 mM) the time evolution of the SP band of the silver particles in such a solution was monitored at different time intervals.

Figure 1A shows the SP band of the silver particle preparation in the presence of 0.002 mM 1 at different times after adding Ag^+ . The increase of the SP band

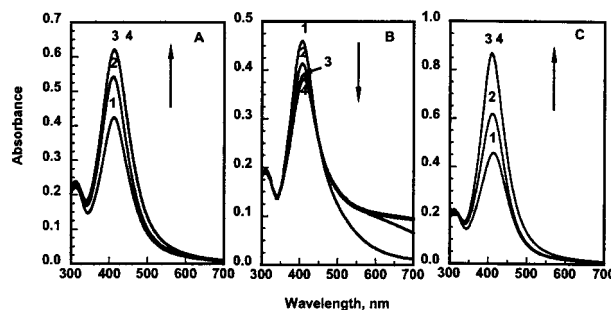


Figure 1. Visible absorption of silver nanoparticles in the presence of (A) 0.002 mM 1, $\lambda_{\text{max}} = 411$ nm, (B) 0.002 mM 2, $\lambda_{\text{max}} = 411$ nm, and (C) 0.014 mM 2, $\lambda_{\text{max}} = 411$ nm at 4 (trace 1), 10 (trace 2), 40 (trace 3), and 70 min (trace 4) after adding 20 mM Ag^+ into 60 °C DMF. The reaction temperature was changed to 20 °C 10 min after adding Ag^+ . The arrow indicates the evolution of the SP band intensity in the period investigated.

Table 1. Average Silver Particle Size Measured by PCS under Different Preparative Conditions

entry	capping ligand	concn, mM	particle diameter, nm
1	perthiolated β -CD, 1	0.002	38 ± 38
2	monothiolated β -CD, 2	0.002	N/A
3	monothiolated β -CD, 2	0.014	63 ± 27
4	perthiolated cavitand, 3	0.002	82 ± 65
5	toluenethiol, 4	0.008	N/A

intensity around 411 nm indicates the continuous formation of silver particles.¹⁷ After 10 min, the reaction was quenched by switching the temperature back to 20 °C. The overlapping of the last two spectra (traces 3 and 4 in Figure 1A), obtained 30 and 60 min after quenching the reaction, indicates that the process of particle generation and growth has stopped. This was also verified by photon correlation spectroscopic (PCS) measurements.¹⁸ The very small wavelength change (< 2 nm) in the maximum of the SP band during the process of silver particle formation indicates that surface modification by compound 1 starts almost simultaneously with particle formation. The symmetric character of the SP band, with a nearly unchanged width in Figure 1A, implies that the size of the nanoparticles is pretty uniform,¹⁹ a point that was confirmed by our PCS measurements. Under these conditions, the final average particle size was 38 nm (entry 1 in Table 1).

When 0.002 mM monothiolated β -CD is used as the capping ligand under the same reaction conditions, the process of silver particle formation is quite different. The SP band of the silver particles reaches a maximum development in the first few minutes and then decreases as shown in Figure 1B. At the same time the absorption intensity in the 600–700 nm region keeps increasing (traces 2, 3, and 4) during the preparation. This indicates that after the rapid formation of silver particles in the first few minutes, the silver particles begin to aggregate and flocculate.²⁰ In other words, the kinetics of surface attachment of compound 2 to the silver particle surfaces is not fast enough to prevent the aggregation and subsequent flocculation of the growing particles. Inceas-

(12) Tolueneithiol was purchased from Aldrich and used without further purification. For the synthesis of perthiolated cavitand, see: Bryant, J. A.; Blanda, M. T.; Vincenti, M.; Cram, D. J. *J. Am. Chem. Soc.* 1991, 113, 2167. For the synthesis of monothiolated β -CD, see: Fujita, K.; Ueda, T.; Imoto, T.; Tabushi, I.; Toh, N.; Koga, T. *Bioorg. Chem.* 1982, 11, 72. For the synthesis of perthiolated β -CD, see our previous publication: Rojas, M. T.; Koniger, R.; Stoddart, J. F.; Kaifer, A. E. *J. Am. Chem. Soc.* 1995, 117, 336. All compounds were fully characterized before use.

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ing the concentration of compound 2 in the preparation accelerates the surface modification process, leading to more stable silver particles as shown in Figure 1C. When 0.014 mM of monothiolated β -CD is used under identical reaction conditions as before, we observed a pattern (Figure 1C) for the evolution of the silver SP band similar to that shown in Figure 1A. However, the average particle size in this case was 63 nm (entry 3 in Table 1), which is considerably larger than that obtained with the same total thiol concentration using ligand 1. The metal nanoparticles are formed through the initial nucleation of reduced metal atoms followed by particle growth processes.²¹ Sometimes, thiol molecules may form complexes with reacting metal ions diminishing the concentration of the free ions and subsequently hindering the nucleation process.²² This is not a significant concern in the present study because the concentration of thiol molecules was set to be at least one thousand times lower than that of the silver ions in the solution. Under the conditions of our experiments, adsorption of thiol molecules onto the particle surface (capping) during the process of particle formation is believed to be the key step that will determine the final particle size. Faster adsorption prevents particle growth more effectively, and therefore, smaller particles will result. Although the total concentrations of thiol groups in the preparations corresponding to entries 1 and 3 were the same, perthiolated β -CD (1) is more efficient at capping the emerging silver particles than the monothiolated β -CD analogue (2).

Cavitands constitute another class of very interesting macrocyclic host molecules,²³ which have been also investigated in our group²⁴ and others.²⁵ The perthiolated cavitand (compound 3) and the much simpler, model compound, toluenethiol (compound 4) were selected for similar experiments in order to test whether our findings could be extended to other types of macrocyclic ligands. The evolution of the silver SP band in the presence of 0.002 mM of perthiolated cavitand (compound 3) after adding 20 mM of Ag^+ is shown in Figure 2A. As with compound 1, the silver particles were stabilized by the perthiolated cavitand and no aggregation or flocculation

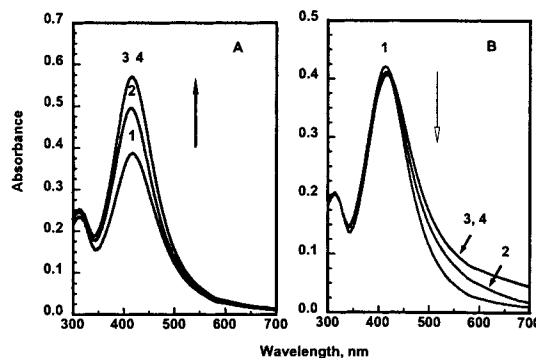


Figure 2. Visible absorption of silver nanoparticles in the presence of (A) 0.002 mM 3 and (B) 0.008 mM 4 at 4 (trace 1), 10 (trace 2), 40 (trace 3), and 70 min (trace 4) after adding 20 mM Ag^+ into 60 °C DMF. The reaction temperature was switched to 20 °C 10 min after adding Ag^+ . The arrow indicates the evolution of the SP band intensity in the period investigated.

was detected. The average particle size measured by PCS was 82 nm, which is significantly larger than the particles stabilized by perthiolated β -CD. Although both the perthiolated cavitand and β -CD are macrocyclic molecules, perthiolated β -CD is more efficient at capping the silver nanoparticles, leading to smaller particles. This is probably due to the fact that 1 has seven thiol groups per molecule while 3 only has four.

While a 0.002 mM concentration of compound 3 can successfully stabilize the silver particles, 0.008 mM of toluenethiol (same total thiol concentration) does not stabilize the silver particles under the same reaction conditions. Figure 2B shows the time evolution of the silver SP band. The increase in absorbance in the 600–700 nm region indicates the aggregation and flocculation of the silver particles after their formation.

In conclusion, our data demonstrate that macrocyclic, multidentate thiol ligands are more effective at capping emerging silver nanoparticles, leading to smaller and more stable particles than monodentate thiol ligands with similar structures. This sort of “macrocyclic effect” probably results from an increased probability of surface attachment for the multidentate thiols, as they possess more functional groups capable of initiating their chemisorption process. In addition to this, once the surface attachment starts, their multidentate character must lead to a more robust, multipoint anchoring of the ligand. Therefore, this macrocyclic effect in metal nanoparticle capping reactions may have both kinetic and thermodynamic origin.

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