

Dendrimer–cyclodextrin assemblies as stabilizers for gold and platinum nanoparticles

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Aqueous assemblies of adamantyl-derivatized poly(propylene imine) (PPI) dendrimers and β -cyclodextrin (β -CD) have been used as nanoreactors in the preparation of gold and platinum nanoparticles in water. These particles have been formed by the reduction of aurate or platinate anions in the presence of the generation 4 ($4\cdot(\beta\text{-CD})_{32}$) and 5 ($5\cdot(\beta\text{-CD})_{40}$) assemblies. Lower generation assemblies did not provide stable nanoparticles. A kinetic model is proposed in which the particles form inside the dendrimer assemblies owing to preferred nucleation as a result of the electrostatic attraction between the polycationic core and the metallate anions. The persistent shape of the adamantyl-derivatized dendrimers and the dense shell of adamantyl- β -CD complexes provide a kinetic barrier for nanoparticle escape thus prolonging their lifetime. Exchange of the dendrimers for a cationic disulfide provided stable, water-soluble metal nanoparticles without change of their size distribution.

Introduction

Metal nanoparticles are of interest for their application in a wide variety of areas such as catalysis, optical devices, nanotechnology, and biological sciences.¹ Several routes towards both water-soluble and water-insoluble metal nanoparticles have been developed over the past years. Stabilization by micelles,² polymers³ and small organic ligands⁴ is common as well as the gas-phase cluster formation method.⁵

Dendrimers such as the well known poly(amido amine) (PAMAM) dendrimers⁶ provide multiple metal coordinating sites, either in the dendritic core or at the periphery. For this reason native and modified PAMAM dendrimers have been used to stabilize nanoparticles of copper,⁷ gold,^{8–11} silver,^{8a} palladium,¹² and platinum.^{7a,12} Also poly(propylene imine) (PPI) dendrimers¹³ stabilize copper¹⁴ and palladium.¹⁵ Very recently, an elegant method was reported in which dendritic Frechet-type wedges having a single metal-coordinating group were used to control the sizes of gold nanoparticles.¹⁶

In this paper we describe how supramolecular dendritic

assemblies of β -cyclodextrins and PPI dendrimers function as water-soluble nanoreactors for the size-selective fabrication of gold and platinum nanoparticles. Recently,¹⁷ we reported such well-defined aqueous assemblies of β -cyclodextrin and intrinsically water-insoluble adamantyl-terminated PPI dendrimers 1–5, having 4 to 64 adamantyl endgroups (Fig. 1).¹⁸ These assemblies form upon complexation of the adamantyl groups by the β -cyclodextrins in water, driven by hydrophobic interactions.¹⁹ The observed stoichiometries are $1\cdot(\beta\text{-CD})_4$, $2\cdot(\beta\text{-CD})_8$, $3\cdot(\beta\text{-CD})_{16}$, $4\cdot(\beta\text{-CD})_{32}$, and $5\cdot(\beta\text{-CD})_{40}$. At low pH, the dendrimers are highly positively charged because of protonation of the tertiary core amines,²⁰ and the assemblies function as supramolecular hosts for the negatively charged fluorescent probe 8-anilinonaphthalene-1-sulfonate (ANS). This observation prompted us to load the dendritic assemblies with aurate and platinate anions *via* electrostatic interaction and to subsequently reduce the metallates in order to form metal nanoparticles. Stabilities and size effects are discussed as a function of dendrimer generation, and a kinetic model for nanoparticle nucleation and growth is presented.

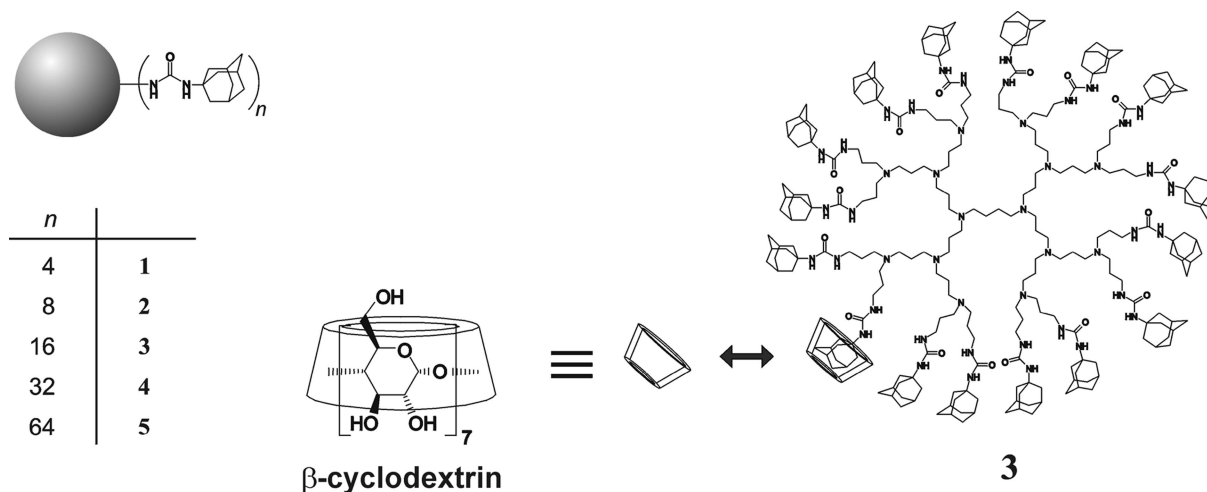


Fig. 1 Poly(propylene imine) dendrimer generations 1–5, solubilized by β -cyclodextrin.

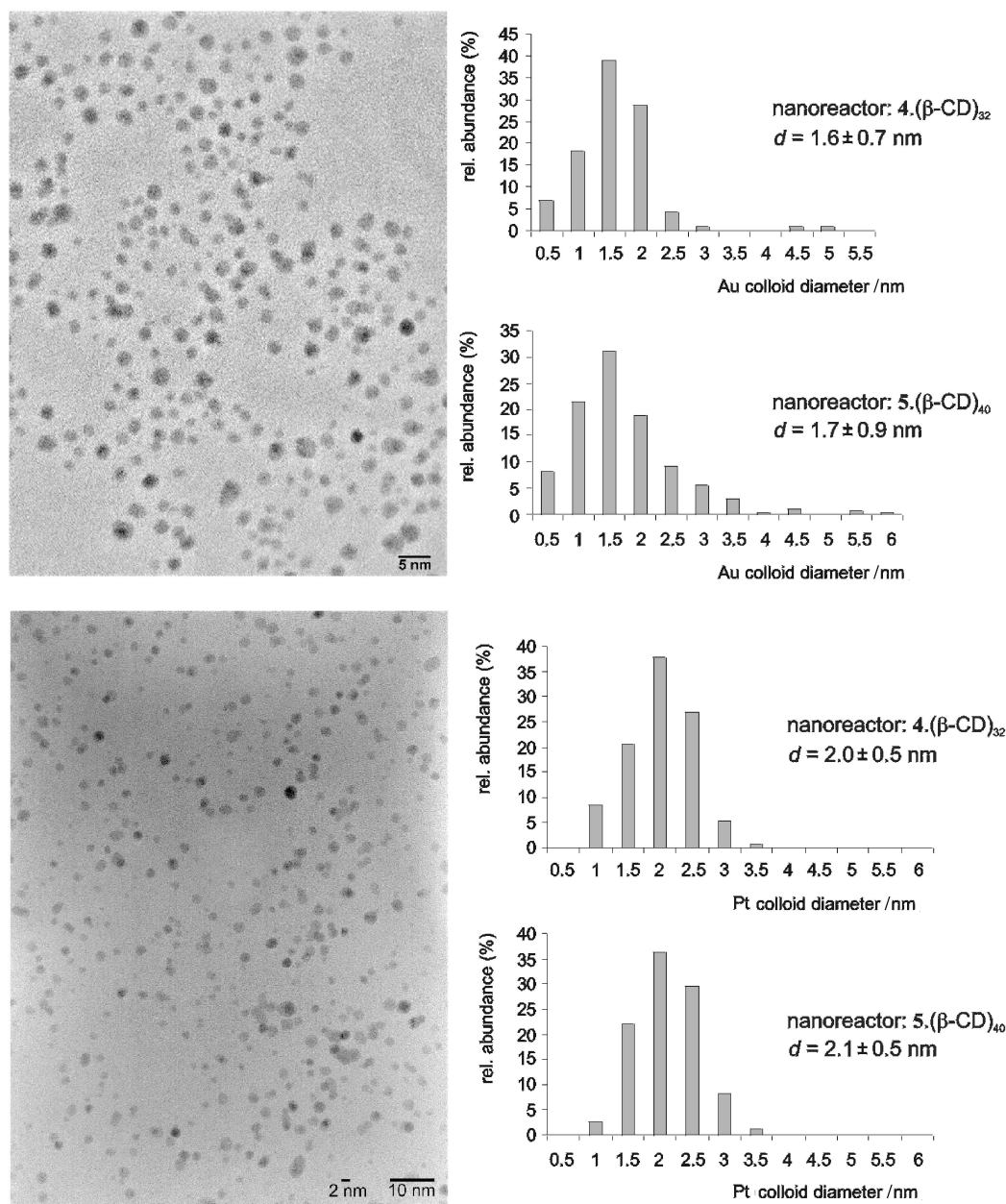


Fig. 2 TEM image of gold (top) and platinum (bottom) nanoparticles stabilized by the $5\cdot(\beta\text{-CD})_{40}$ assembly and size distributions of colloids stabilized by $4\cdot(\beta\text{-CD})_{32}$ and $5\cdot(\beta\text{-CD})_{40}$ (amine : metal = 2 : 1, H_2O , $T = 25^\circ\text{C}$).

Results and discussion

Equivalent amounts of $\text{HAuCl}_4\cdot 3\text{H}_2\text{O}$ or PtCl_4 were added to the fully protonated dendrimer- $\beta\text{-CD}$ assemblies (amine : metal = 2 : 1) in water at pH 1.²¹ Driven by electrostatic interaction, AuCl_4^- or PtCl_6^{2-} ions are attracted by the polycationic dendritic assemblies and subsequently reduced by addition of a freshly prepared aqueous solution of NaBH_4 . In the presence of the $1\cdot(\beta\text{-CD})_4$, $2\cdot(\beta\text{-CD})_8$, and $3\cdot(\beta\text{-CD})_{16}$ assemblies (having 2, 6, and 14 tertiary core amines, respectively), the addition of NaBH_4 resulted in immediate precipitation of large, black metal aggregates.²² In contrast, in the presence of the $4\cdot(\beta\text{-CD})_{32}$ and $5\cdot(\beta\text{-CD})_{40}$ assemblies (having 30 and 62 tertiary core amines, respectively), the color of the solutions changed from pale yellow to brownish red in the case of gold and to brown in the case of platinum, indicative of the formation of metal nanoparticles.

TEM photographs of the freshly prepared solutions confirmed the formation of nanosized gold and platinum colloids stabilized by the $4\cdot(\beta\text{-CD})_{32}$ and $5\cdot(\beta\text{-CD})_{40}$ assemblies (Fig. 2). The sizes of the Pt colloids ($d = 2.0 \pm 0.5$ and 2.1 ± 0.5 nm

for $4\cdot(\beta\text{-CD})_{32}$ and $5\cdot(\beta\text{-CD})_{40}$, respectively) are slightly larger than for the Au colloids ($d = 1.6 \pm 0.7$ and 1.7 ± 0.9 nm for $4\cdot(\beta\text{-CD})_{32}$ and $5\cdot(\beta\text{-CD})_{40}$, respectively). The dispersity of the Au and Pt particles is significantly lower than the dispersities of most of the earlier reported dendrimer-stabilized nanoparticles. For both metals the difference in particle size of the colloids stabilized by $4\cdot(\beta\text{-CD})_{32}$ and $5\cdot(\beta\text{-CD})_{40}$ is not significant. The UV-vis absorption spectrum of the gold colloid solutions showed a plasmon band at approx. 525 nm as a shoulder, typical for small gold nanoparticles ($d < 5$ nm).^{7b,10} As expected,²³ no surface plasmon band was observed in the UV-vis spectrum of the platinum colloids. These Au and Pt nanoparticles were stable for 1–2 days at room temperature in daylight. Stored at 4°C in the dark, the particles were stable for approximately one week.

Cationic polyelectrolytes containing ammonium functionalities are known to stabilize gold nanoparticles through electrostatic compensation of the negative surface charge due to adsorbed chloride or bromide ions.^{24–26} Although definite proof is difficult to obtain, we assume our metal particles to reside *inside* the dendrimer- $\beta\text{-CD}$ assemblies. First, the

Table 1 Core volume, core diameter, and dendritic surface area of the $3\cdot(\beta\text{-CD})_{16}$, $4\cdot(\beta\text{-CD})_{32}$, and $5\cdot(\beta\text{-CD})_{40}$ assemblies (the numbers are calculated using data from ref. 17)

Assembly	$d_{\text{core}}/\text{nm}$	$V_{\text{core}}/\text{nm}^3$	$V_{\text{empty}}/\text{nm}^3$	$d_{\text{empty}}/\text{nm}$	$A_{\text{shell}}/\text{nm}^2$	$A_{\text{open}}/\text{nm}^2$
$3\cdot(\beta\text{-CD})_{16}$	2.6	9.2	6.5	2.3	43	17 (40%)
$4\cdot(\beta\text{-CD})_{32}$	3.3	19.5	13.8	3.0	62	9 (15%)
$5\cdot(\beta\text{-CD})_{40}$	4.1	36.1	24.4	3.6	85	0 (0%)

dendrimer periphery does not contain metal particle stabilizing functionalities. Second, owing to the bulkiness of the adamantyl groups even in the absence of the β -cyclodextrins these dendrimers are rigid, persistently globular entities.²⁷ Due to this rigidity, the adamantyl-terminated PPI dendrimers are not capable of exposing their cores. Finally, the β -cyclodextrins complexed to the adamantyl groups form an insulating, almost 1 nm thick rigid shell around the dendritic core,¹⁷ which may act as a kinetic barrier for a metal particle for migrating out of an assembly.

We have compared the diameters of the gold and platinum colloids with the diameters (d_{empty}) corresponding to the free volume (V_{empty}) theoretically available for colloidal growth inside the dendritic poly(ammonium) cores of the $4\cdot(\beta\text{-CD})_{32}$ and $5\cdot(\beta\text{-CD})_{40}$ assemblies. V_{empty} is the difference between the total dendrimer core volume (V_{core}) and the volume occupied by the core skeleton. The volume occupied by the core material was calculated from the molecular weight of the poly(propylene imine) part ($\text{C}_{88}\text{H}_{176}\text{N}_{30}$, $\text{C}_{184}\text{H}_{368}\text{N}_{62}$, and $\text{C}_{376}\text{H}_{752}\text{N}_{126}$ for **3**, **4**, and **5**, respectively), assuming an approximate density of 1 g cm^{-3} . V_{core} was calculated from the core diameter d_{core} , obtained from molecular modeling data reported previously.^{28,29} The values of V_{core} , V_{empty} , and d_{empty} (calculated from V_{empty}) for $3\cdot(\beta\text{-CD})_{16}$, $4\cdot(\beta\text{-CD})_{32}$, and $5\cdot(\beta\text{-CD})_{40}$ are summarized in Table 1.

Obviously, the voids in the dendrimer cores do not form a single, spherical cavity. Nevertheless, the interior is rather liquid-like,²⁹ allowing accommodation of a spherical nanoparticle. The numbers given in Table 1 can therefore be used as a rough measure of particle sizes that may fit into the dendrimer interiors. The comparison of d_{empty} with the experimentally observed diameters of the colloids $<3.0\text{--}3.5\text{ nm}$ (see Fig. 2) suggests that the colloids fit inside the dendritic pockets of **4** and **5**. Furthermore, the open surface area (A_{open} , Table 1)¹⁷ in the shells of the assemblies shows that $5\cdot(\beta\text{-CD})_{40}$ and $4\cdot(\beta\text{-CD})_{32}$ have a much denser shell (0% and 15% of open space, respectively) than the $3\cdot(\beta\text{-CD})_{16}$ assembly (40% of open space). These numbers suggest that $3\cdot(\beta\text{-CD})_{16}$ and lower generation assemblies do not provide kinetic barriers to prevent the colloids from migrating out of the dendritic cores and subsequently aggregating into larger metal clusters.

We propose a kinetic model according to which the formation of the dendrimer-stabilized colloids may occur (Fig. 3).

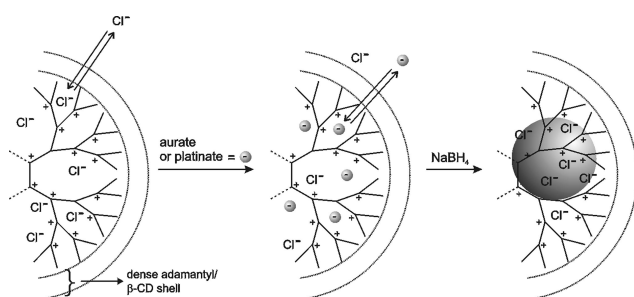


Fig. 3 Growth model for the formation of gold and platinum nanoparticles stabilized by $4\cdot(\beta\text{-CD})_{32}$ and $5\cdot(\beta\text{-CD})_{40}$.

High local concentrations of aurate or platinate anions are present inside the dendrimers and upon addition of NaBH_4 nucleation of particle growth will predominantly take place inside the dendrimers. Rapid influx of aurate or platinate

anions from the surrounding solution driven by electrostatic interaction favors particle growth at the nucleated sites. The growth is limited to a certain cut-off value by the dense rigid shells of the assemblies, which give rise to relatively narrow particle size distributions.

Gold nanoparticles with increased stability (> 6 months) were obtained by addition of the water-soluble disulfide 12,12'-dithiodidodecylamine³⁰ to the freshly prepared dendrimer-stabilized gold colloid solutions. Upon addition of the disulfide, the color changed to brown. This may be due to a change of the particle coordination, as Fig. 4 shows that the particle size is not influenced by the exchange process. We have proven by ^1H NMR spectroscopy that the disulfide indeed binds to the gold nanoparticles. Upon coordination to the gold, the intensity of the triplet corresponding to the methylene group adjacent to the sulfur decreases strongly. Only the signal corresponding to the free disulfide remains detectable.

Most likely, some disulfide molecules are able to penetrate the cyclodextrin–adamantyl shell and coordinate to the gold nanoparticle. This reduces the binding by the core ammonium groups, accelerating the dissociation of the particle from the dendritic core, which spontaneously also occurs in a few days (see above). Thus, empty dendrimers are obtained, as well as thiolate-protected gold nanoparticles with their usual, prolonged nanoparticle lifetime.

Conclusions

In conclusion, we have shown that protonated PPI dendrimers can be used for the size selective synthesis of gold and platinum nanoparticles. Supramolecular assemblies of these dendrimers and β -cyclodextrins act as nanoreactors and provide kinetic barriers for nanoparticle escape because of their dense shell of supramolecular adamantyl- β -CD complexes. Redistribution of the anions during the nanoparticle growth phase prevents the formation of purely monodisperse colloids, but attaining larger metallate loadings may overcome this limitation.

Experimental

Preparation of dendrimer-stabilized colloids

The nanoparticles were prepared at $20\text{ }^\circ\text{C}$ using doubly distilled water (Q2). Under vigorous stirring, 0.5 mL of a 0.01 M $\text{HAuCl}_4\cdot 3\text{H}_2\text{O}$ or PtCl_4 solution in water was slowly added to 2 mL of an aqueous dendrimer solution at $\text{pH} = 1$, with $[\beta\text{-CD}]/[\text{adamantane}] = 2$. Amine : metal ratios of 2 : 1 or 1 : 1 were applied. Subsequently, 0.5 mL of a 0.1 M solution of NaBH_4 in water was added at once, while stirring vigorously. After reduction, clear solutions were obtained of $\text{pH} = 2$.

Preparation of thiol-stabilized gold colloids

The gold colloids were prepared as described above. Subsequently, one equivalent (relative to Au^{III}) of 12,12'-dithiodidodecylamine,³⁰ dissolved in water at neutral pH , was added to the deeply red mixture, while stirring vigorously. Upon addition of the disulfide, the color changed to brown.

Analyses

Transmission electron microscopy (TEM) images of the dendrimer-stabilized gold and platinum nanoparticles and of

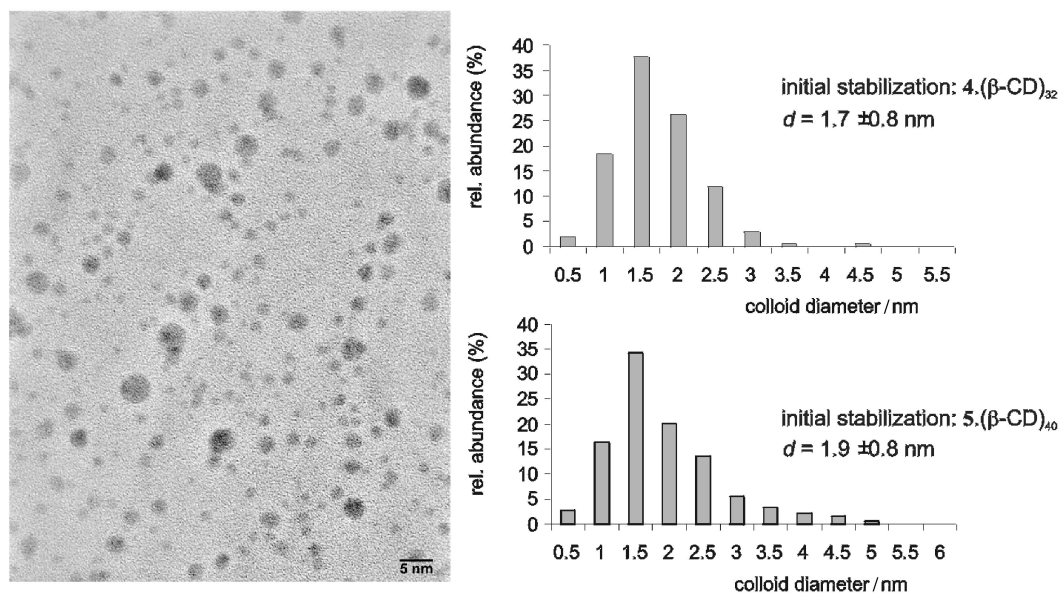


Fig. 4 TEM image of gold colloids stabilized by 12,12'-dithiodidodecylamine and size distributions of the colloids initially stabilized by 4·(β-CD)₃₂ and 5·(β-CD)₄₀ (amine : gold = 2 : 1, H₂O, pH = 2, T = 25 °C).

the thiol-stabilized gold colloids were collected on a Philips CM 30 Twin FTEM, fitted with Kevex delta plus X-ray dispersive electron spectroscopy (EDX) and a Gatan model 666 PEELS, operating at 300 kV. Samples were prepared by drop-casting a drop of an aqueous colloid solution onto a 200 mesh copper grid, and left to dry for 15 min at 20 °C.

UV-vis spectra of strongly diluted nanoparticle solutions were recorded at 25 °C using a Hewlett Packard 8452A diode array spectrophotometer. The spectra were corrected for the background absorbance of the solvent (H₂O).

¹H NMR spectra of bis(ω-aminododecyl) disulfide and the dendrimer- and thiol-stabilized gold nanoparticles were recorded at 25 °C in D₂O at pD = 7 at 300 MHz on a Varian Inova 300 NMR spectrometer.

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