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Gold Nanoparticles Stabilized by Glycodendrimers: Synthesis and Application to the Catalytic Reduction of 4-Nitrophenol

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Air-stable gold nanoparticles stabilized by glycodendrimers (AuDSNs) in water were prepared in the presence of a reducing agent, $NaBH_4$. A UV/Vis spectroscopy study demonstrates that no spontaneous reduction of Au^{3+} ions occurs in the presence of glycodendrimers. The AuDSNs were characterized by UV/Vis spectroscopy and transmission electron microscopy (TEM). TEM images show that the AuDSNs were very small (average diameter: 2.6 nm). The catalytic activity of these AuDSNs was evaluated for the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) by $NaBH_4$ monitored by UV/Vis spectroscopy. Studies of the reduction reaction reveal that the rate constant depends on the concentration of 4-NP.

Introduction

Recent advances in the development of nanoparticles (NPs) have led to potential applications in several areas of nanosciences including photophysics, biological sensing, medicine, and catalysis.[1] The growing interest in NPs might be explained by the improvement of their methods of preparation: the use of organic additives such as dendrimers allows one to control the size of the NPs by preventing agglomeration, increase the stability, and influence the solubility in organic and aqueous media of the formed NPs.[2] Dendrimers[3] offer advantages over other stabilizers in that they have well-defined, compartmentalized structures in the nanometer-sized range, narrow polydispersity, and globular morphology (applicable to higher-generation dendrimers), which enable them to entrap and stabilize NPs, especially if they contain heteroatoms in their interiors. The most common pathway to dendrimer-encapsulated nanoparticles is the reduction of transition-metal ions within the dendrimers.[2] In addition to these aspects (solubility, stabilization, protection), the dendrimers confer specific functionalities on the NPs for potential applications. In catalysis, NPs stabilized by dendrimers present advantages of both homogeneous and heterogeneous catalysts: (i) the size and the solubility of the NPs is controlled by the architecture of the dendrimer, (ii) the accessibility to the NP is determined by the surface of the dendrimer, and (iii) the recyclability often is facile. In this context, and as a continuation of our study on dendrimer-stabilized metal NPs,[4] we wish to disclose the facile "click" preparation of air-stable glycodendrimer-stabilized Au nanoparticles (DSNs) that contain 1,2,3-triazolyl linkages, the role of which has been evidenced in the formation of gold nanoparticles (AuNPs) templated by dendrimers and polymers.[5] Then, the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) was selected as a model reaction[6,7] to evaluate the catalytic potential of these new DSNs. Nitrophenols are among the most toxic and hazardous micropollutants, thus their degradation is really challenging for environmental purposes.[8]

AuNPs have found potential applications in various fields (catalysis, optics, electronics, biology, medicine) owing to their unique spectroscopic and chemical properties.[9] In the field of catalysis, AuNPs have witnessed a burst of interest since the discovery by Haruta and co-workers of their low-temperature catalyst properties in the oxidation reaction of carbon monoxide by dioxygen.[10] In the literature, a number of works have dealt with the contribution of AuNPs stabilized by dendrimers in various redox reactions including oxidation of alcohols,[11] and reduction of nitrobenzene[12] and 4-NP.[13] Mainly AuNPs stabilized by commercial poly(amido amine) (PAMAM) and poly(propyleneimine) (PPI) dendrimers are described in these works.

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However, our interest is in the intradendritic 1,2,3-triazole ligands formed by "click" functionalization of dendrimers that coordinate transition-metal cations undergoing further reduction to catalytically very active metal NPs. The use of amphiphilic glycodendrimers for AuNP stabilization addresses important current problems, such as aqueous catalysis and biological recognition.[14] In these fields, the presence of carbohydrates at the periphery of the dendrimers confers to AuNPs key properties such as reduced toxicity, water solubility, chiral surface for asymmetric induction,[15] and capacity to form supramolecular interactions with proteins such as lectins that are useful in nanomedicine.[14g] Although glycodendrimers are a rich area[16] and the use of dendrimers decorated by C6 sugars in enantioselective catalysis has already been described,[16a,16b] to the best of our knowledge the literature on pentoses decorating dendrimers remains scarce.[4,16g,16h] From an ecological and economic perspective, pentoses are abundant, renewable, and low-cost molecules from agricultural resources.[17] The use of pentoses to decorate dendrimers is therefore part of a sustainable development strategy and might contribute to lower their price. Therefore, readily available pentose-decorated dendrimers are utilized in the present article to generate "click" dendrimer-stabilized AuNPs that show remarkable catalytic activity.

Results and Discussion

The dendritic core used for pentose dendrimer synthesis results from the classic mild CpFe$^+$-induced (Cp = cyclopentadienyl) nona-allylation of mesitylene followed by visible-light photo-decomplexation, hydrosilylation of the double bonds with chloromethyldimethylsilane, and nucleophilic chloride substitution by azide.[18] The Cu^{I}-catalyzed click reaction yielding the nona-pentose hydrophilic dendrimer has been reported,[4] and this dendrimer is now used for Au^{III} complexation. The most common pathway to DSNs is the reduction of such transition-metal ions within the dendrimers. Therefore, the water-soluble glycodendrimer containing 9 terminal modified xylose branches and $HAuCl_4$ (9 equiv.) were mixed together in water for 20 min under air, to provide enough time for Au^{3+} ions to be encapsulated into the dendrimer interior. The stoichiometry corresponds to the number of triazole rings in the glycodendrimer, as in previous studies.[4,5] Then, an aqueous solution of $NaBH_4$ was added dropwise to reduce the Au^{3+} ions to zerovalent Au (Scheme 1).

As demonstrated by the optical extinction spectrum (Figure 1), the formation of AuDSNs stabilized by the glycodendrimers was instantaneous, and a pink-brown solution was obtained. The optical extinction spectrum of the AuDSNs shows a broad band at around λ = 520 nm corresponding to the plasmon band of AuNPs.[9] As reported earlier in the literature and because of the low generation

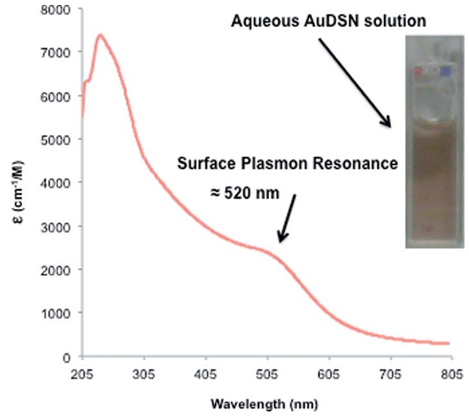
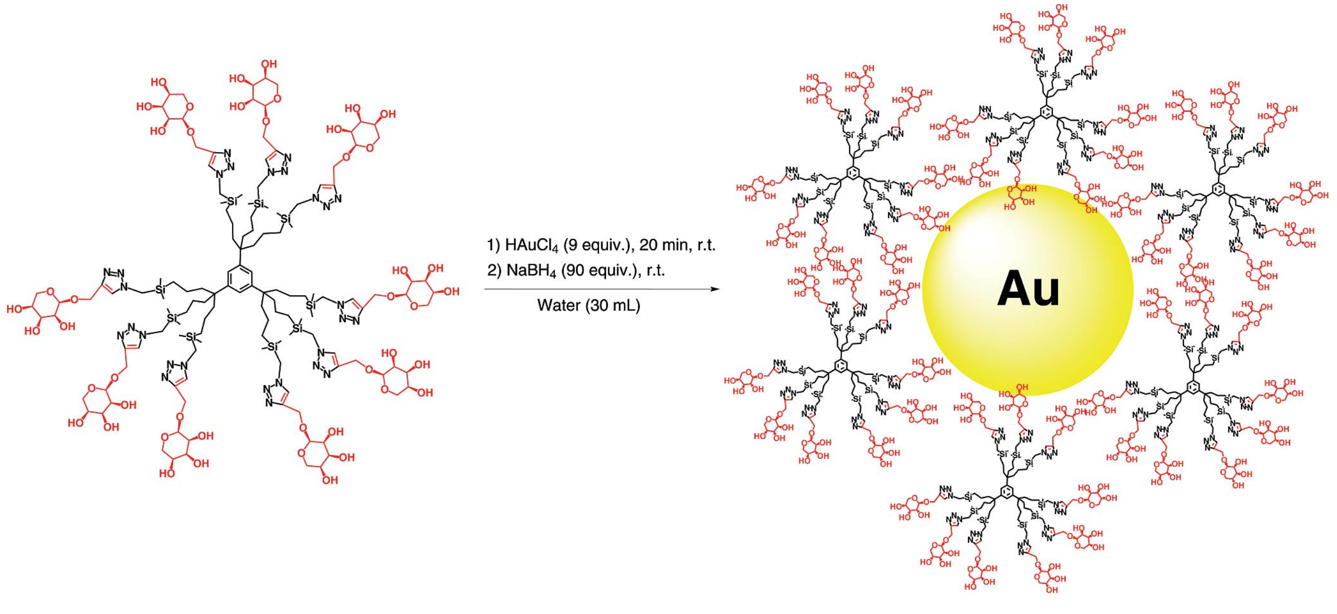


Figure 1. Optical extinction spectrum of AuDSNs in solution in water recorded with glycodendrimer in water as the blank.



Scheme 1. Preparation of monometallic AuDSNs stabilized by glycodendrimers.

of the glycodendrimer that is used, the AuNPs are stabilized by several small dendrimers at the surface (DSNs).[2e,2f,5a]

A few groups have reported the formation of AuNPs stabilized by dendrimers without any external reductant.[5b,14d–14f] In particular, Esumi and co-workers pointed out the role of hydroxy groups of peripheral sugar balls of poly(amidoamine)dendrimers reducing Au^{3+} ions and yielding AuNPs after 90 min with the observation of a plasmon band at 520 nm.[14d] These hydroxy groups were oxidized to carbonyl groups, which was confirmed by the comparison of FTIR spectra of gold particles/sugar balls and the apparition of a new band near 1732 cm^{-1} corresponding to carbonyl groups. These results led us to study the reducing power of our glycodendrimers through various analytical techniques such as UV/Vis, FTIR, and fluorescence spectroscopy.

A dilute aqueous solution containing a mixture of the glycodendrimer and $HAuCl_4$ was followed by UV/Vis spectroscopy, over a period of 24 hours (Figure 2). In the aqueous solution before adding the glycodendrimer, $HAuCl_4$ shows a strong absorption band at $\lambda = 217$ nm and a shoulder at 290 nm owing to ligand-to-metal charge transfer (LMCT) between the metal and chloro ligands.[2d] 40 min after adding the glycodendrimer, the shoulder at 290 nm increased but no growing Au plasmon shoulder appeared with time in this spectrum (even after 24 h, Figure 2, c), contrary to other reports with other glycodendrimers.[14d–14f]

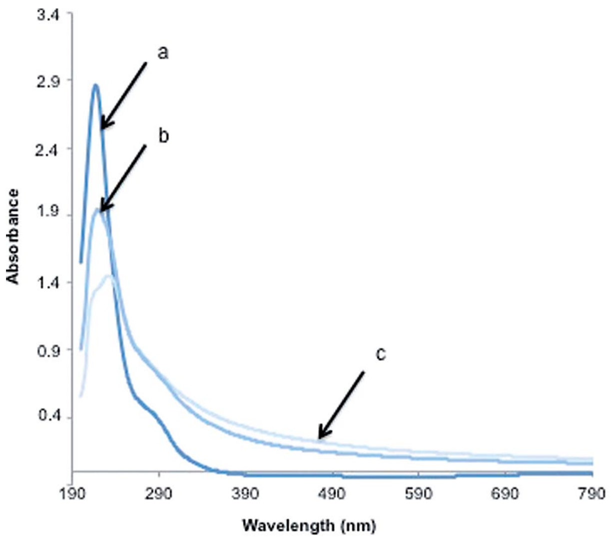
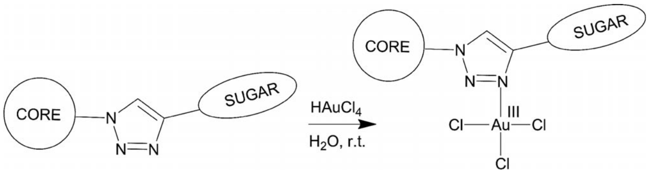


Figure 2. UV/Vis spectra: (a) $HAuCl_4$ in water; (b) $HAuCl_4$ and the glycodendrimer after 40 min; (c) $HAuCl_4$ and the glycodendrimer after 24 h. UV/Vis spectra presented in (b) and (c) were recorded with glycodendrimer in water as the blank.

The increase in absorbance at $\lambda = 290$ nm may be explained by the complexation of Au^{III} to the triazole rings. Complexation of Au^{III} to the 1,2,3-triazolyl ring in water at room temperature (Scheme 2) has already been suggested by Bortoluzzi and co-workers[19] and by us.[5b]



Scheme 2. Schematic representation of the complexation of Au^{III} to the 1,2,3-triazolyl ring.

FTIR spectra of solutions containing $AuCl_4^-$ (9 equiv.)/glycodendrimer (1 equiv.) in water after 1 and 20 h of stirring showed the absence of carbonyl groups. The fluorescence spectrum was also recorded after 24 h (excitation at 510 nm, from a xenon arc source), but no signal indicating the formation of Au^0 particles was detected. All these results are consistent with a lack of reduction of Au^{3+} ions to Au^0 at room temperature in water after 24 h in the presence of the glycodendrimers used in this study. The absence of reducing power of these glycodendrimers might be attributed to the absence of free hemiacetal functions in the peripheral sugars.

The TEM analysis of the AuDSNs stabilized by the glycodendrimers is shown in Figure 3. The particles have an average size of (2.6 ± 0.4) nm (over 100 counted NPs), which corresponds to 541 Au atoms per NP, calculated by using the equation $n = 4\pi r^3/3V_g$, in which n is the number of Au atoms, r is the radius of the Au nanoparticle determined by TEM, and V_g is the volume of one Au atom (17 Å^3).[20]

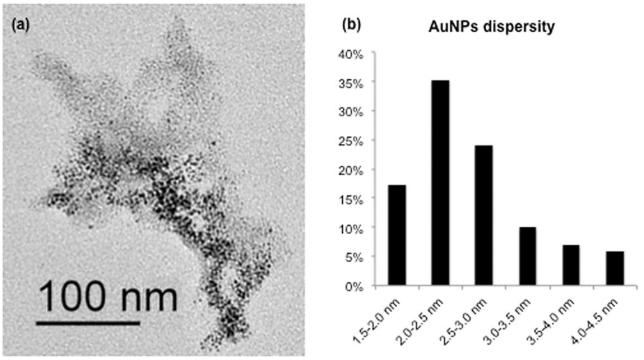
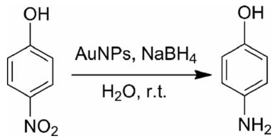


Figure 3. (a) TEM analysis of AuDSNs stabilized by the glycodendrimers; (b) Size distribution of AuNPs stabilized by the glycodendrimers.

The most efficient NPs in catalysis have small sizes (<10 nm). Indeed, when the particle size decreases, the proportion of the number of atoms on the surface, corners, and edges, which are expected to be the catalytically active ones, increases.[1b,1d] Therefore, it appeared interesting to check the catalytic activity of these very small AuDSNs, and the reduction of 4-NP to 4-AP was chosen. Various groups have already reported the reduction of 4-NP catalyzed by Au dendrimer-stabilized nanoparticles, mainly with commercial PAMAM and PPI dendrimers.[21]

The reduction of 4-NP (1 equiv.) to 4-AP in water in the presence of $NaBH_4$, using AuDSNs stabilized by glycodendrimers as catalyst was monitored in a spectrophotometric cell in water at 25 °C by the disappearance of the strong absorption band at λ_{max} = 405 nm (ε = 18450 cm^{-1} M^{-1}). The appearance of this band corresponds to the instantaneous formation of 4-nitrophenolate in the presence of $NaBH_4$. The formation of 4-AP is characterized by the increase of an absorption band at 300 nm (Scheme 3).



Scheme 3. Reduction of 4-NP to 4-AP in water in the presence of $NaBH_4$ using glycodendrimer-stabilized AuNPs as catalyst.

Figure 4a shows the successive UV/Vis spectra corresponding to the reduction of 4-NP using 10 mol-% of AuNPs and 100 equiv. of $NaBH_4$, and Figure 4 (b), the plot of –ln (C_t/C_0) (C_t = concentration at time t, C_0 = concentration at t = 0) as a function of time (in seconds), which allows the rate constant (k) to be determined. As previous studies showed, there is an induction time, t_0, that corresponds, in the assumption of a Langmuir–Hinshelwood mechanism, to "an activation or restructuration of the metal surface by nitrophenol"[22] before the reduction actually starts. Then, the reaction follows pseudo-first order as usually accepted.[21] The rate constant k was calculated to be 2.4×10^{-3} s^{-1}.

Table 1 shows a comparison of the average diameter and the rate constants obtained in the reduction of 4-NP, between the AuDSNs synthesized in the present study and AuDSNs stabilized by PAMAM-NH_2 and PPI dendrimers (2nd generation) reported in the literature.[21a] For all the data in Table 1, AuDSNs are stabilized by dendrimers of low, comparable generation at their surface. G2-PAMAM-NH_2 and G2-PPI dendrimers have 8 branches at the surface and the present glycodendrimer has 9 branches. From Table 1 it appears that the AuDSNs prepared in the present study have comparable catalytic activity and diameter to those reported with PPI and PAMAM dendrimers.

Table 1. Comparison with selected results from the literature obtained with AuNPs stabilized by dendrimers.

Dendritic system	Average diameter [nm]	Mol-% AuNPs	[4-NP] [10^{-4} M]	$NaBH_4$ [equiv.]	k [10^{-3} s^{-1}]
G0-Glyco	2.6	10	1	100	2.4
G2-PAMAM-NH_2[21a]	3.7	10	1	100	1.74
G2-PPI[21a]	3.6	10	1	100	1.23

To optimize this reaction and to deepen our understanding of our catalytic system we varied the molar percentage of AuDSNs (mol-%) and the concentration of 4-NP ([4-NP]) and kept constant the amount of $NaBH_4$ at 81 equiv. instead of 100 equiv. All the results are summarized in Table 2 (see Figures S1–S3 in the Supporting Information for details).

Table 2. Reduction of 4-NP to 4-AP with AuDSNs using $NaBH_4$ (81 equiv.).

Entry	Mol-% AuNPs	[4-NP] [10^{-4} M]	k [10^{-3} s^{-1}]
1	0.2	6.2	6.5
2[a]	0.2	6.2	–[b]
3[c]	0	6.2	–[b]
4	0.2	2.5	1.3
5	0.5	1.5	1.1
6	2	1.5	1.8

[a] The reduction of 4-NP was conducted in the presence of 0.2 mol-% Au taken from a freshly prepared solution containing AuNPs, following the procedure described in the Experimental Section but without glycodendrimer. [b] Not determined because too slow. [c] The reduction of 4-NP was conducted in the presence of the same concentration of glycodendrimer as used for entry 1 but without Au.

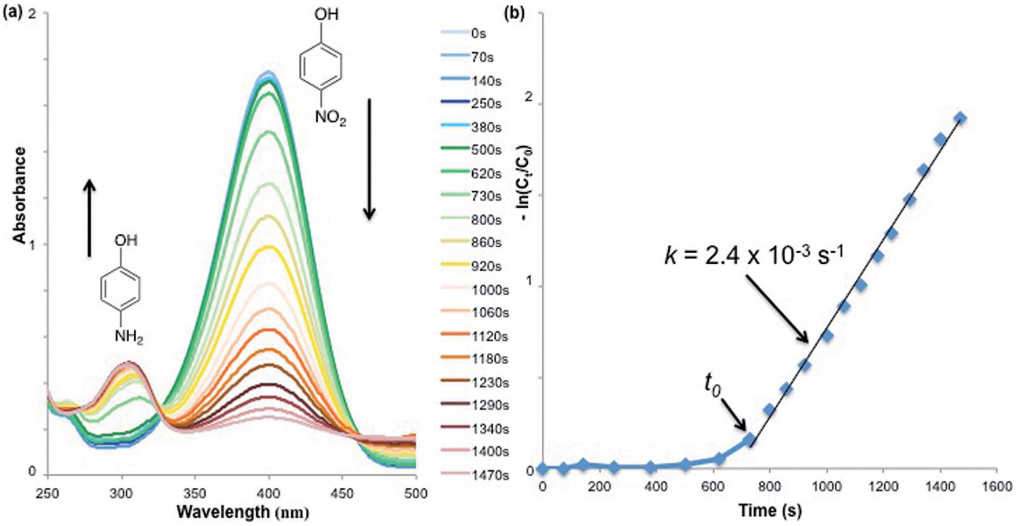


Figure 4. (a) Successive spectra monitoring the reduction of 4-NP (1×10^{-4} M) in the presence of AuDSNs (10 mol-%) stabilized by glycodendrimers. (b) Plot of –ln (C_t/C_0) as a function of time (s).

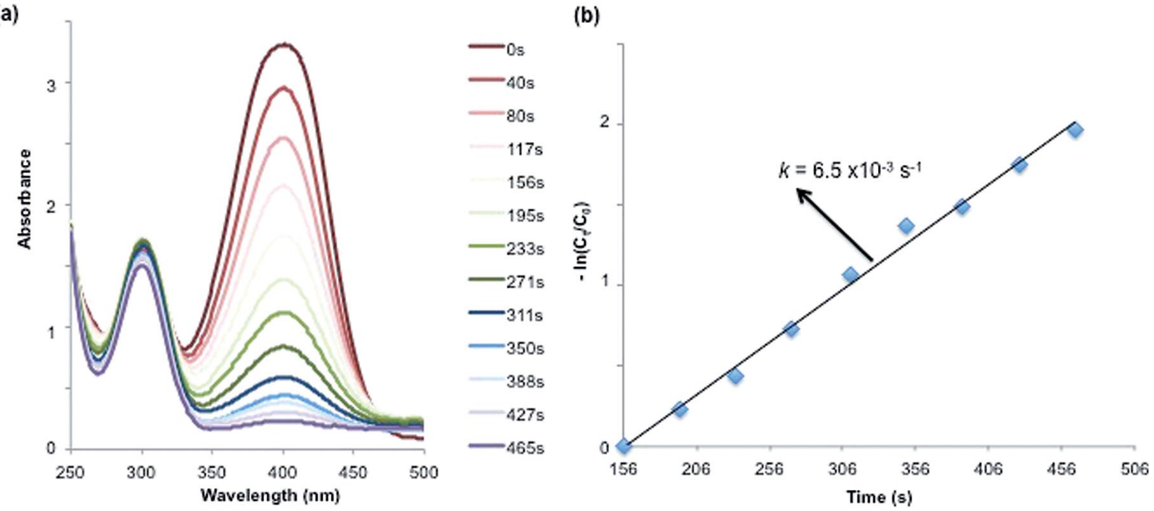


Figure 5. (a) Successive spectra monitoring the reduction of 4-NP (6.2×10^{-4} M) in the presence of AuDSNs (0.2 mol-%) stabilized by glycodendrimers. (b) Plot of $-\ln(C_t/C_0)$ as a function of time (s).

In the presence of 0.2 mol-% of metal, with a concentration of 6.2×10^{-4} M 4-NP, the reaction was almost completed in 465 s, which corresponds to a k value of 6.5×10^{-3} s^{-1} (Table 2, entry 1, Figure 5). The [4-NP] used in this experiment led to starting UV/Vis spectra (from 0 to 117 s) in which absorbances are greater than 2. With respect to the Beer–Lambert law, it was considered that these results were not relevant, and therefore they were not used to build up the kinetic plots. The UV/Vis spectrum at 156 s was treated as the initial spectrum for this reduction.

The same reaction performed in the absence of the glycodendrimer, with AuNPs formed only with $NaBH_4$, led after 20 min to UV/Vis spectra in which absorbances are still greater than 2 for the absorption band of 4-nitrophenolate at λ = 405 nm (Table 2, entry 2, for example, after 24 min, the absorbance at 405 nm is 3.60). This result shows the advantage of using AuNPs stabilized by glycodendrimers containing 1,2,3-triazolyl linkages for the reduction of 4-NP. Since Schmitzer and co-workers showed that glycodendrimers without AuNPs catalyze the reduction of cyclohexylphenyl ketone to alcohol,[16b] we carried out the reduction of 4-NP (6.2×10^{-4} M) only in the presence of the glycodendrimer (Table 2, entry 3). After 20 min, no reduction of the 4-NP was observed. When the concentration of 4-NP was decreased to 2.5×10^{-4} M, the reaction was completed after 1219 s with a k value of 1.3×10^{-3} s^{-1} (Table 2, entry 4). Increasing the quantity of catalyst from 0.5 to 2 mol-% led to an increase of the reaction rate (Table 2, entry 5 and 6), as expected. However, the variation of this parameter seems to have less effect on the reaction rate than the concentration of 4-NP.

Conclusion

The decoration of dendrimers with pentose allows them to be solubilized in water at low cost, to combine them with metal ions such as Au^{III} and further to metallic nanoparticles, and to enable them to catalyze reactions that need to be carried out in water. In the course of our study on the preparation of these AuDSNs, we have discarded the idea that Au^{3+} might be spontaneously reduced to Au^0 in presence of the glycodendrimers. These DSNs are catalytically active in the reduction of 4-NP to 4-AP by $NaBH_4$ and show similar catalytic activity and diameter with previously comparable AuDSNs synthesized with PAMAM and PPI dendrimers. These results show the advantage of the triazole linkages in water-soluble glycodendrimers for the mild AuNP stabilization and their good catalytic activity.

Experimental Section

General Data: All chemicals were used as received. Glycodendrimer was synthesized as described in the literature.[4] Particle size was determined by TEM by using a JEOL JEM 1400 (120 kV) microscope. TEM samples were prepared by deposition of the nanoparticle suspension (10 µL) on a carbon-coated microscopy copper grid. The IR spectra were recorded on an ATI Mattson Genesis series FTIR spectrophotometer. UV/Vis absorption spectra were measured with a Perkin–Elmer Lambda 19 UV/Vis spectrometer.

Procedure for the Preparation of AuNPs: A 3.1×10^{-4} M aqueous solution of glycodendrimer (1.4 mL) was added to deionized water (25.6 mL), followed by the addition of a freshly prepared 2.6×10^{-3} M aqueous solution of $HAuCl_4$ (1.5 mL). The resulting mixture was then stirred for 20 min under air and a 2.6×10^{-2} M $NaBH_4$ aqueous solution (1.5 mL) was added dropwise, provoking the formation of a pink-brown color corresponding to the reduction of Au^{3+} ions to Au^0 and AuNPs formation. The UV/Vis spectrum of AuNPs (Figure 1) was recorded with a blank solution of glycodendrimer (1.45×10^{-5} M) in water.

Investigation of the Interaction Between the Glycodendrimer and the Au^{III} Salt: The following aqueous solutions were prepared: (A)

HAuCl$_4$ (1.37×10^{-4} M), (B) HAuCl$_4$ (1.37×10^{-4} M) + glycodendrimer (1.53×10^{-5} M) and (C) glycodendrimer (1.53×10^{-5} M). The UV/Vis spectrum of solution A is presented in Figure 2 (a). The evolution of solution B was monitored by UV/Vis spectroscopy over a period of 24 h; UV/Vis spectra were recorded after 40 min and after 24 h using solution C as a blank and these spectra are presented in Figure 2 (b and c).

General Procedure for the Reduction of 4-NP: 4-NP (1 equiv.) was mixed with NaBH$_4$ (81 equiv.) in water under air, then the solution containing the freshly prepared AuNPs was added. After adding NaBH$_4$, the solution changed from light yellow to dark yellow owing to the formation of the 4-nitrophenolate ion. Then, this solution loses its dark yellow color with time after addition of AuNPs. The reaction was monitored by UV/Vis spectroscopy.

Supporting Information (see footnote on the first page of this article): UV/Vis spectra of the reduction of 4-nitrophenol by AuNPs stabilized by glycodendrimers and the corresponding plots of $-\ln(C_t/C_0)$ as a function of the time can be found in the Supporting Information.

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