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# Encapsulation and Stabilization of Gold Nanoparticles with "Click" Polyethyleneglycol Dendrimers

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***Abstract:*** Water-soluble arene-cored "clicked" and non-"clicked" dendrimers terminated by 27, 81, and 243 triethyleneglycol (TEG) tethers (respectively generations G0, G1, and G2) have been synthesized and shown to form dendrimer-encapsulated gold nanoparticles (DEAuNPs) and dendrimer-stabilized gold nanoparticles (DSAuNPs). The dendrimers have been characterized by IR, $^{1}$H NMR, $^{13}$C NMR, size-exclusion chromatography, elemental analysis, MALDI-TOF mass spectroscopy, DOSY NMR, and dynamic light scattering. The AuNPs have been generated and stabilized by these PEGylated dendrimers using a variety of reduction modes, including $NaBH_4$ in methanol, various single-electron metallocene-type reductants, and even in the absence of additional reductants. The active role of the "clicked" triazole rings, dendrimer generation, stoichiometry of Au precursor, and nature of the reductant and of the solvent are delineated, leading to DSAuNPs with the G0 dendrimer and smaller DEAuNPs with the G1 and G2 dendrimers. Altogether, AuNPs in the size range from 1.8 to 42 nm were formed and characterized by transmission electron microscopy (TEM), high resolution TEM (HRTEM) and UV−vis spectroscopy. Both 1,2,3-triazole and PEGylated Percec-type dendrons are required in the dendrimer structure for the stabilization of AuNPs upon $NaBH_4$ reduction of $HAuCl_4$ in methanol. On the other hand, in the absence of other reductant in water, only PEGylated Percec-type dendrons in dendrimers were found to be indispensable, because of their semicavitand shape, for the spontaneous reduction of $HAuCl_4$ and stabilization of DSAuNPs.

## Introduction

Substrate encapsulation by dendrimers[1] is a major property of dendrimer chemistry that has potential applications in catalysis,[2] photophysics,[3] materials science[4] and nanomedicine.[5] One of the most remarkable examples of dendritic encapsulation is that of transition-metal nanoparticles (NPs) that was disclosed more than a decade ago using polyamidoamine (PAMAM) dendrimers,[6] then polypropyleneimine (PPI) dendrimers.[7] Crooks and his group,[8] among others,[7–9] have demonstrated the enormous potential of this concept in catalysis under various "green" conditions and have shown that the dendrimer plays the role of a nanoreactor and nanofilter.[8] In particular, NP encapsulation has been applied to many transition metals including the use of a redox reaction between a NP and other metal cations.[2] However, the studies of dendrimer-encapsulated NPs (DENs) have essentially concerned the PAMAM and PPI dendrimer families that are commercial, with the main exception

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of Yamamoto's phenylazomethine dendrimers whose rigidity brings about new specific features for properties of phenylazomethine-DENs in materials science.[9]

It has recently been shown that dendrimers assembled by click chemistry[10] can coordinate and electrochemically recognize various transition-metal cations,[11] and that such palladodendritic complexes can be reduced to DEPdNPs that have remarkable catalytic properties.[12] Such a strategy does not work in the same way for an approach to arene-cored DEAuNPs,[13] and the investigation toward a rationalization of the syntheses toward this goal is presented and generalized here. Besides encapsulation, exodendrimer stabilization is also well-known,[14] and this alternative has also been searched with arene-cored dendrimers[15] constructed using a Newkome-type 1 → 3 connectivity.[16] Moreover, our goal was to stabilize and *inter alia* encapsulate AuNPs using polyethyleneglycol-terminated dendrimers,[17] because of their biocompatibility[17] and the applications of AuNPs in nanomedicine.[18]

A major finding in this work is that Percec-type triethyleneglycol (TEG) tethers[19] are not only tolerated for the synthesis of DEAuNPs and DSAuNPs but they are even required for this purpose in this new arene-cored dendrimer series, and under certain circumstances they allow the AuNP formation. The key additional role of the intradendritic 1,2,3-triazole rings, formed by "click" reaction, on the AuNP formation and stabilization is also shown.

## Results

The synthesis of two series of arene-cored, PEG terminated dendrimers of three generations has been carried out. For both series, the dendrimer syntheses start by $CpFe^+$-induced nonaallylation of mesitylene[15] followed by photolytic decomplexation[20] and Newkome-type 1 → 3 connectivity.[16] The first series of dendrimers was synthesized using "click" chemistry (dendrimers **4**, **5** and **6**, Scheme 1), and the other one using the Williamson reaction (dendrimers **9**, **10** and **11**, Scheme 2) in order to graft PEG dendrons at the periphery of the dendrimers. The AuNPs are stabilized by these PEGylated dendrimers, synthesized by "click" chemistry (**4**, **5** and **6**), in methanol using $NaBH_4$ as the reductant. The PEG-terminated (dendronized) dendrimers (**4**−**6** and **9**−**11**) also allowed the reduction of $Au^{III}$ to $Au^0$ in water without the presence of an additional reductant. The shape and the size of the AuNPs have been studied by UV−vis spectroscopy and transmission electron microscopy (TEM) and the kinetics of formation and size variations of the


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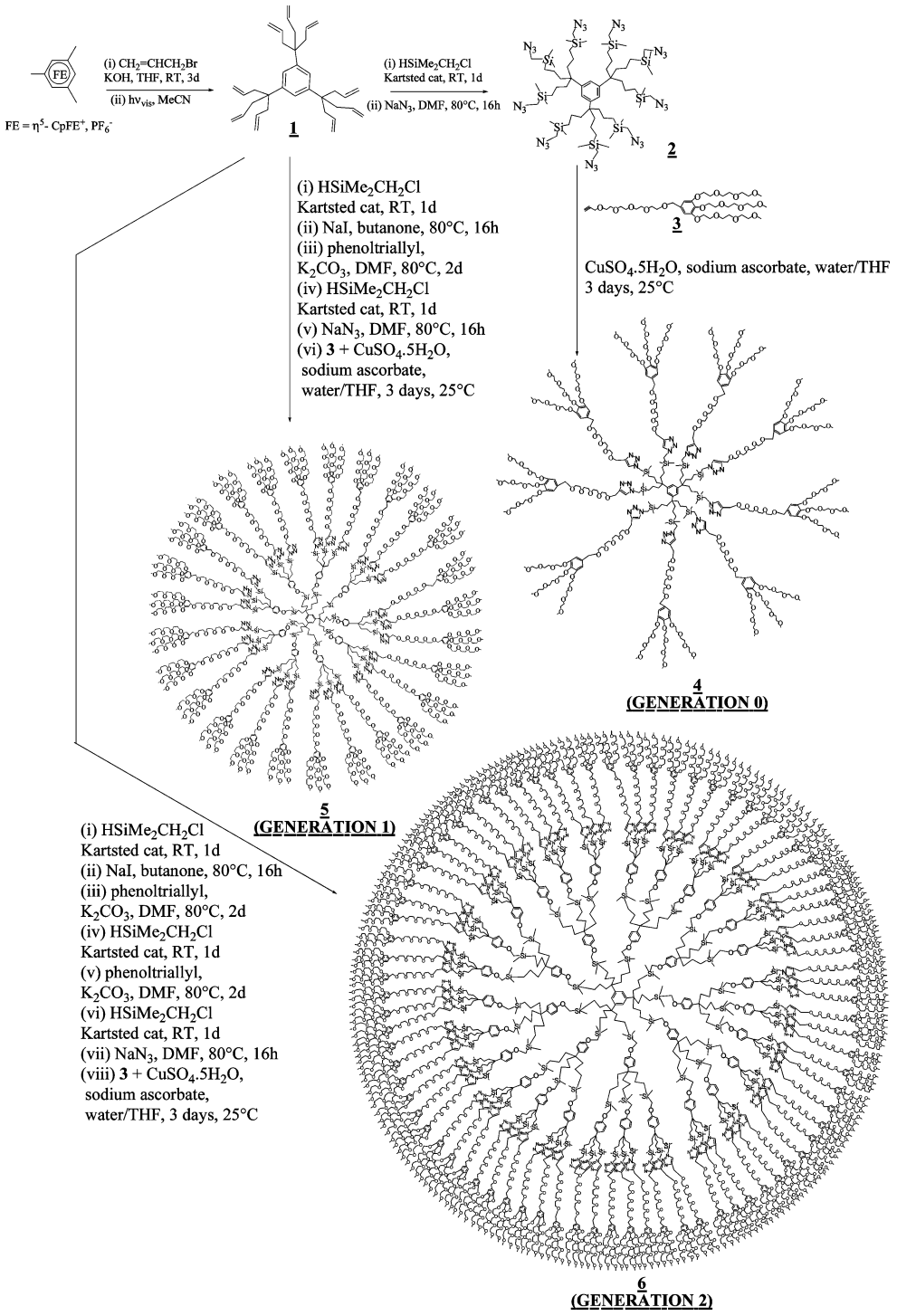
***Scheme 1.*** Synthesis of the Three Generations of "Click" Dendrimers **4**, **5** and **6**




AuNPs have been examined when the number of equivalents of $HAuCl_4$ added per dendrimer was increased. The influence of the nature of the reductant used in methanol, that is, $NaBH_4$ or an electron-reservoir organometallic sandwich complex, was also studied, and the role of the standard redox potential of the reductant on the AuNP formation was finally scrutinized. Overall, the synthesis of AuNPs stabilized or encapsulated by PEGylated dendrimers is detailed.

**1. Synthesis and Characterizations of Dendrimers 4, 5 and 6 Synthesized by "Click" Chemistry.** The synthesis of three generations of arene-cored dendrimers with 1→ 3 connectivity (**4**, **5** and **6**) terminated with 27, 81 and 243 PEG tethers ($G_0$ to $G_2$) is shown in Scheme 1. The dendritic precursors with 9 chloromethyl and azido groups were reported earlier.[15] The Newkome-type 1 → 3 connectivity[16] was continued by the Williamson reaction between the nonachloromethyl core and a Percec-type dendron.[19] This dendron was synthesized from a modified gallic acid core functionalized at the focal point by a tetraethyleneglycol (TAEG) linker, then by a propargyl group, and on the peripheral tethers by triethylene glycol (TEG) termini (**3**). Finally, the dendrons were linked to the core using the $Cu^I$-catalyzed "click" reaction between the terminal alkyne tail and the azido-terminated dendritic core.[11] A stoichiometric amount of $Cu^I$, generated using $CuSO_4$ and sodium ascorbate, has been

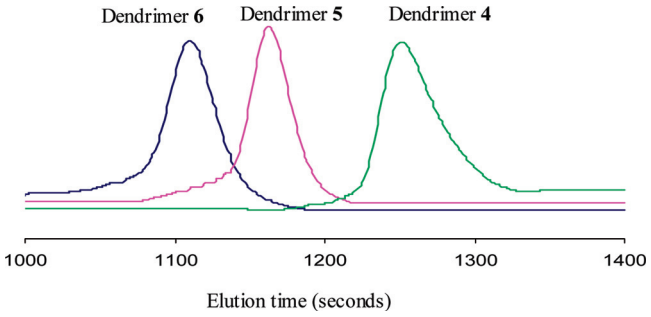



***Figure 1.*** Size Exclusion Chromatography of the three generations of the "click" dendrimers **4**−**6** containing polyethyleneglycol tethers (PDI = 1.02 ± 0.01).

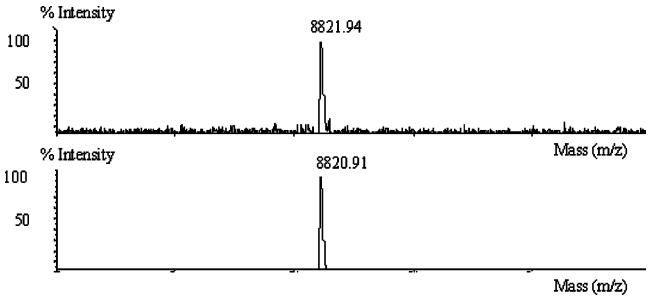



***Figure 2.*** MALDI-TOF mass spectrum of the dendrimer **4**. Calcd for $C_{414}H_{741}O_{153}N_{27}Si_9$: 8798; found: 8821.25 (MNa).

used, because dendritic metal encapsulation considerably slows down the click reaction or inhibits it,[11,21] especially with large dendrimers. The dendrimers of generation 0 (**4**, 27 TEG termini) to 2 (**6**, 243 TEG termini) were synthesized in this way in nearly quantitative yields (92−95%), and characterized by IR, $^1$H and $^{13}$C NMR, size exclusion chromatography (**4**, **5** and **6**, Figure 1), correct elemental analysis (**4**), and MALDI TOF (**4**, major peak at $MNa^+$: calcd 8820.91; found: 8821.24, Figure 2). DOSY NMR and dynamic light scattering give consistent data for dendrimers **4** and **5**, both methods giving a diameter values of 9 ± 1 nm for **4** and 18 ± 2 nm for **5**. For the dendrimer **6**, light scattering provides a diameter value of 20 ± 2 nm (Figure 3, see also the Supporting Information, ESI).

**2. Synthesis and Characterizations of Dendrimers 9, 10 and 11 by the Williamson Reaction.** The syntheses of three generations of the arene-cored, TEG-terminated dendrimers **9**, **10** and **11** with 27, 81 and 243 TEG dendrimers ($G_0$ to $G_2$) are shown in Scheme 2. They start with the same steps as for the syntheses of dendrimers **4**, **5** and **6** (see Scheme 1) until the hydrosilylation step. Then, reaction of the dendrimer core terminated by chloromethylsilyl groups with NaI yields the nonaiodomethylsilyl core (**7**). The Percec-type dendron is functionalized at the focal point by a hydroquinone linker in order to introduce a phenol terminus (**8**). Finally, the dendrons are linked to the core using a Williamson reaction between the terminal phenol tail and the iodomethylsilyl-terminated dendritic core. The dendrimers **9**, **10** and **11** of generation 0 (**9**, 27 TEG termini) to 2 (**11**, 243 TEG termini) were synthesized in this way and characterized by IR, $^1$H and $^{13}$C NMR, size exclusion chromatography (**9**, **10** and **11**), MALDI TOF (**9**, major peak

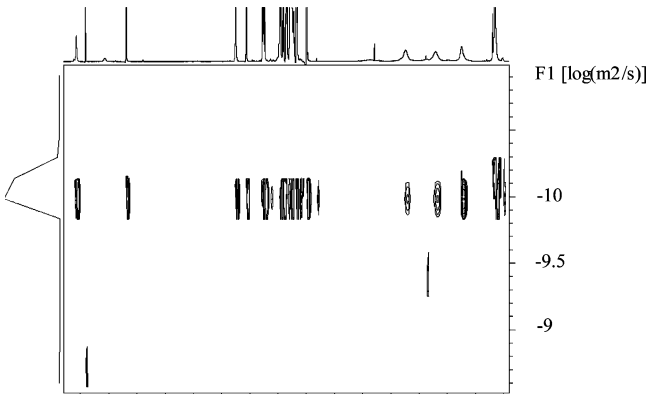



***Figure 3.*** DOSY NMR spectrum of the dendrimer **4**. $D = 1.16\ (\pm 0.1) \times 10^{-10}$ m$^2$/s, Rh = 4.9 (±0.1) nm. D, diffusion coefficient; Rh, hydrodynamic radius.

at $M^+$: calcd 7311.54; found: 7334.47 ($MNa^+$). DOSY NMR and dynamic light scattering provide consistent data for the dendrimers **10** and **11**, both methods giving a diameter values of 13 ± 1.2 nm for **10** and 15 ± 1.5 nm for **11**. For the dendrimer **9**, DOSY NMR yielded a diameter value of 8 ± 0.6 nm (ESI).

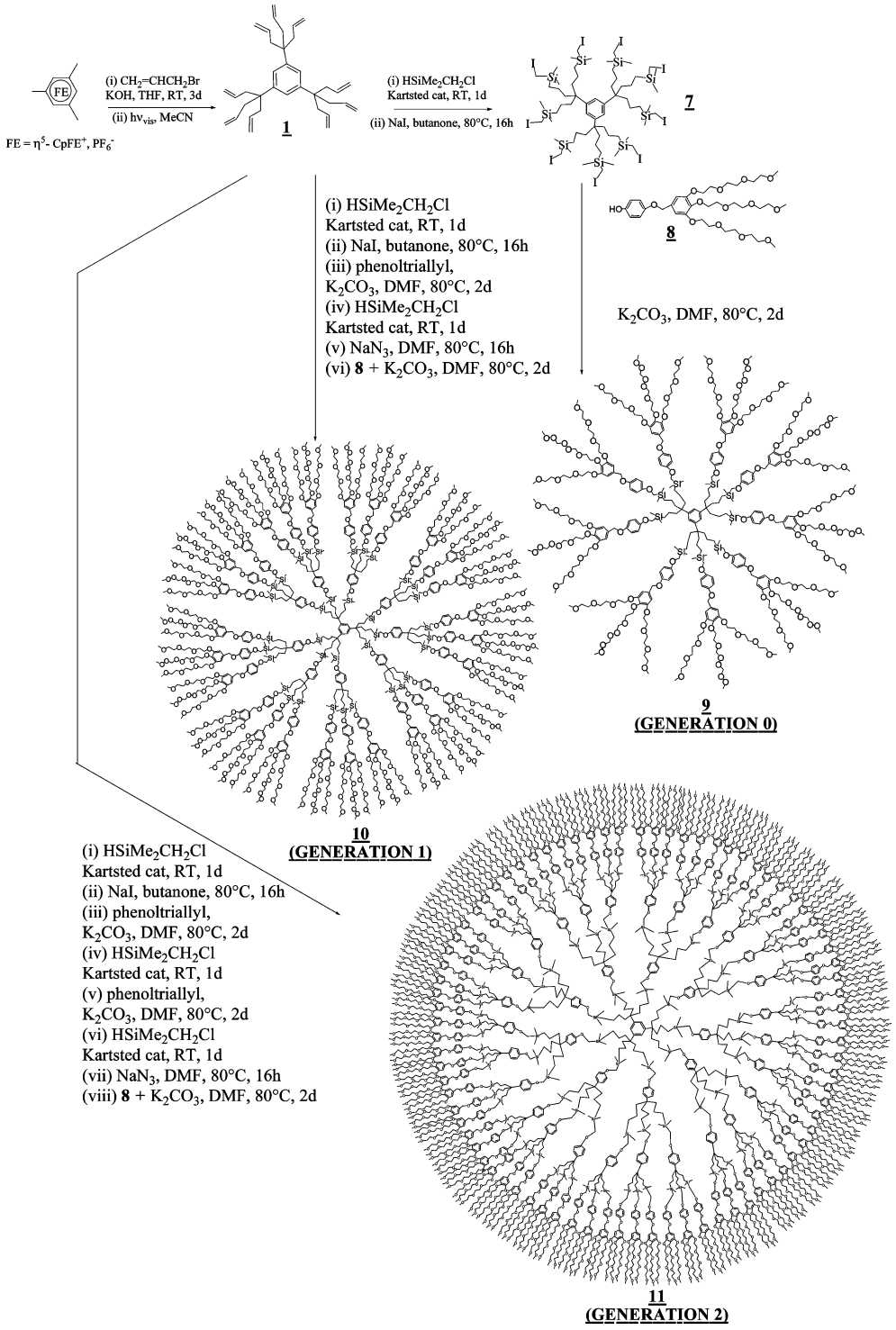
**3. AuNPs Synthesized using $NaBH_4$ and Stabilization in Methanol by the "Click" Dendrimers 4, 5 and 6.** The AuNPs were synthesized by reaction between the "click" dendrimers **4**, **5** and **6,** and a stoichiometric amount of $HAuCl_4$ vs. the dendrimer triazole groups, followed by $NaBH_4$ reduction in methanol. This stoichiometry was selected, because we believed that the AuNPs formed would contain a number of atoms equal to the number of triazole rings in the dendrimer, as with PdNPs. It also allows comparisons between the various procedures used throughout this study. Later, the amount of $HAuCl_4$ was also increased, in order to examine its influence on the AuNP size. The UV−vis spectrum shows a plasmon band at 540 nm for the dendrimer **4**-stabilized AuNPs, but this band is absent in the spectrum of the AuNPs stabilized by the higher-generation dendrimers **5** and **6** (Figure 4). The transmission electron microscopy (TEM) data confirm this trend (Figure 5) showing that the dendrimer **4**-stabilized AuNPs are larger than the dendrimer (4.1 ± 0.5 nm) and cannot be encapsulated in such a small dendrimer that contains only 27 tethers. Thus, several dendrimers **4** are surrounding each AuNP (Figure 6). On the other hand, the larger dendrimers **5** and **6** containing respectively 81 and 243 TEG tethers encapsulate AuNPs of small size (1.9 ± 0.4 nm). Dendrimer **4** has an open structure, and any AuNPs formed therein will start to come out and aggregate into larger AuNPs, while dendrimers **5** and **6** will engulf any forming AuNPs.

**4. Attempts to Stabilize AuNPs in Methanol by Other Dendrimers.** The syntheses and stabilization of AuNPs using a stoichiometric amount of $HAuCl_4$ *per* triazole or Percec-type dendron and $NaBH_4$ reduction in methanol was attempted using six others dendrimers. Three of them, that were reported earlier,[12a] only contain triazole groups and do not contain any PEG (**12**, **13** and **14**), and the three others only contain PEG but no triazole groups (**9**, **10** and **11**).[15b] "Click" dendrimers with 27 and 81 allyl tethers (**13** and **14**) and a "click" dendrimer with 27 phenyl tethers (**12**) were used (Chart 1).

The procedure used for the addition and reduction of $HAuCl_4$ in these dendrimers was the same one as that previously described using a stoichiometric amount of $HAuCl_4$ vs the dendrimer triazole groups. When $NaBH_4$ in methanol was added,

(21) Candelon, N.; Lastécouères, D.; Diallo, A. K.; Ruiz, J.; Astruc, D.; Vincent, J.-M. *Chem. Commun.* **2008**, 741–743.
(22) (a) Komeda, S.; Lutz, M.; Speck, A. L.; Yamanaka, Y.; Sato, T.; Chikuma, M.; Reedijk, J. *J. Am. Chem. Soc.* **1997**, *119*, 2588. (b) Barz, M.; Herdtweck, E.; Thiel, W. R. *Angew. Chem., Int. Ed.* **1998**, *37*, 2262–2265. (c) Chan, T. R.; Holgraf, R.; Sharpless, K. B.; Fokin, V. V. *Org. Lett.* **2004**, *6*, 2853–2856.

***Scheme 2.*** Syntheses of the Three Generations of Dendrimers **9**, **10** and **11** by the Williamson Reactions




the AuNPs were formed, but they precipitated after a few minutes, and AuNPs could never be stabilized (although PdNP could be stabilized[19]).

The dendrimers **9**, **10** and **11** containing respectively 27, 81 and 243 PEG tethers but no triazole ligand were used for comparison (Scheme 2). The procedure used for the addition and reduction of $HAuCl_4$ in this dendrimer was the same as previously described with 27, 81 and 243 equiv of Au per dendrimer. The result was similar to that obtained with the above dendrimers containing only triazole groups, that is, AuNPs immediately precipitated when $NaBH_4$ in methanol was added, and no AuNP could be obtained.

These six experiments support the fact that the presence of both the PEG and triazole groups in the dendrimers **4**, **5** and **6** are essential for the stabilization of AuNPs in methanol, when $NaBH_4$ is used as the reductant.

**5. AuNP Size Variation upon Change of $HAuCl_4$ Stoichiometry in Methanol.** The size variation of the AuNPs synthesized using $NaBH_4$ in methanol was observed in the case of AuNP stabilization with the dendrimer **5** upon change of

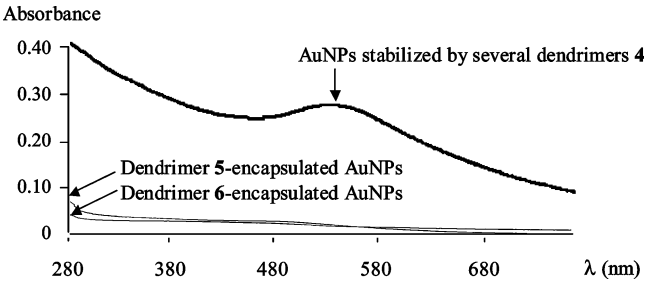



***Figure 4.*** UV−Vis spectra of AuNPs stabilized by several dendrimers **4** and encapsulated by dendrimers **5** and **6**.

stoichiometry of the $HAuCl_4$ precursor. TEM images were recorded (Figure 6) for an increase of the equiv. number of added $HAuCl_4$ from 1 to 20 $Au^{III}$ per intradendritic triazole ligand. All the AuNPs obtained are spherical, and their size is very homogeneous. Moreover, a high resolution TEM was recorded for 7 equiv of $Au^{III}$ per triazole, in order to observe the crystalline structure of the AuNP (Figure 6, *G*). The increase of the number of equiv. $HAuCl_4$ per triazole leads to a variation of the diameter of the AuNPs from 1.9 ± 0.2 nm (1 equiv of $Au^{III}$ per triazole) to 11.3 ± 1 nm (20 equiv of $Au^{III}$ per triazole). From 1 to 10 equiv of $Au^{III}$ per triazole, the AuNP size varies linearly with the number of $HAuCl_4$ equiv added before reaching a plateau at approximately 11 nm (Figure 7). This maximum size is expected, because the AuNPs are stabilized with the dendrimer **5** in an intradendritic way (see section 2), and the diameter of this dendrimer is confirmed by both DOSY NMR and light scattering (18 ± 2 nm). When the number of equivalents of $HAuCl_4$ per triazole is larger than 10, excess $Au^0$ immediately precipitates.

**6. AuNP Synthesis in Water and Stabilization by Dendrimers Terminated by Percec-Type PEG Dendrons in the Absence of External Reductant.** AuNPs were synthesized according to a new protocol, without external reductant and in aqueous dendrimer solution at room temperature. The AuNP were formed by reaction between the TEGylated dendrimers and a stoichiometric amount of $HAuCl_4$ per PEG dendron in water in the dark (i.e., 9 equiv of $HAuCl_4$ per dendrimers **4** and **9**, 27 per dendrimers **5** and **10** and 81 per dendrimers **6** and **11**). The solution became red after a few minutes of stirring. The synthesis of the AuNPs in the presence of dendrimers **9**, **10** and **11** was faster than for the AuNPs obtained with "click" dendrimers **4**, **5** and **6**. This reduction was followed by the evolution of the AuNP plasmon band in UV−vis spectroscopy. For example, the synthesis of the AuNPs with the dendrimer **9**

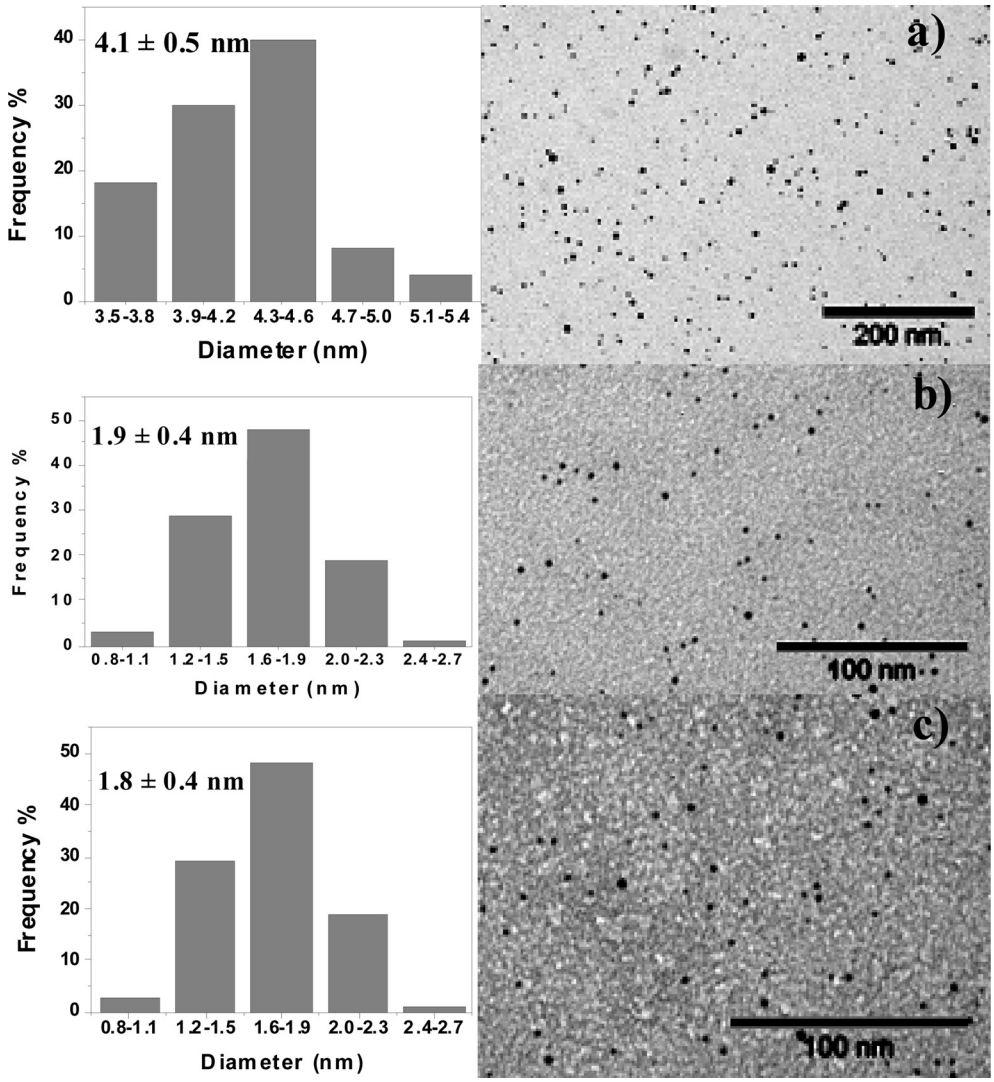



***Figure 5.*** (a) Dendrimer **4**/AuNPs: TEM image and size distribution. (b) Dendrimer **5**/AuNPs: TEM image and size distribution. (c) Dendrimer **6**/AuNPs: TEM image and size distribution.

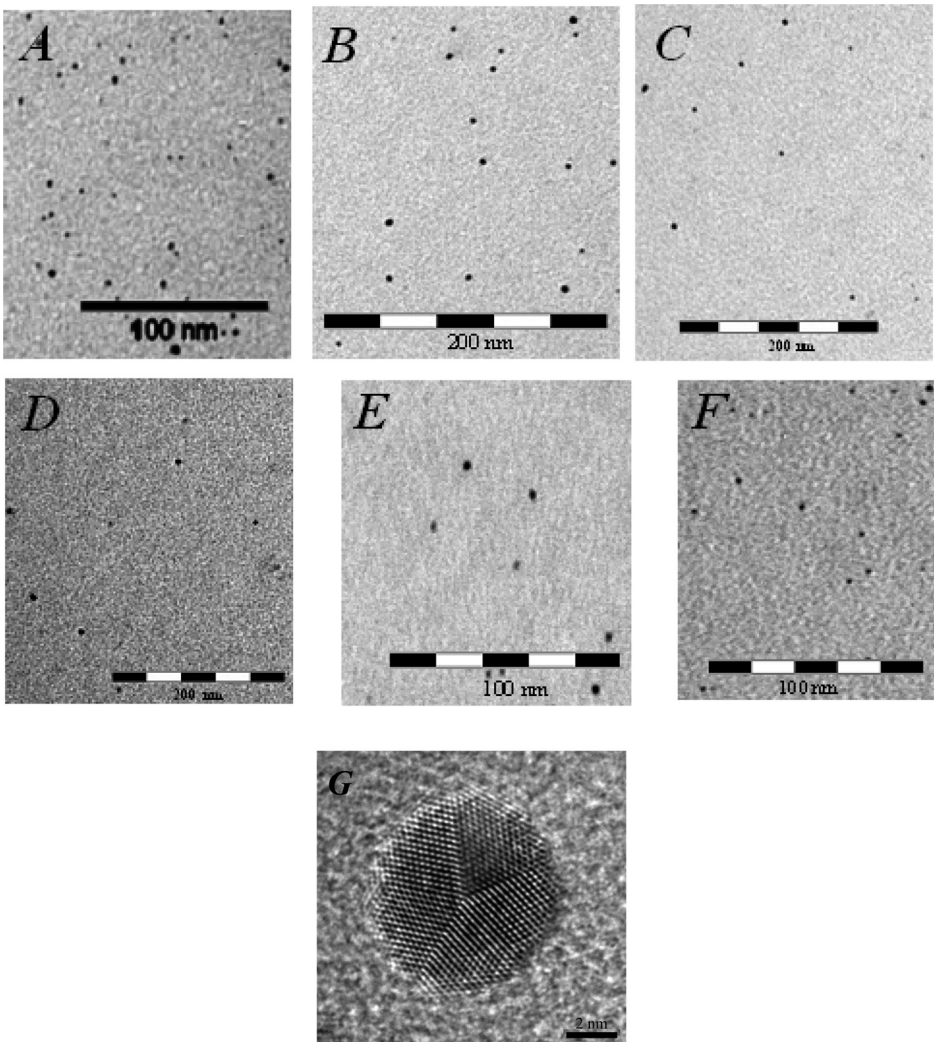



***Figure 6.*** (A) Dendrimer **5** + 1 equiv of $HAuCl_4$ per triazole, diameter = 1.9 (±0.2) nm; (B) dendrimer **5** + 3 equiv of $HAuCl_4$ per triazole, diameter = 3.8 (±0.4) nm; (C) dendrimer **5** + 5 equiv of $HAuCl_4$ per triazole, diameter = 5.3 (±0.5) nm; (D) dendrimer **5** + 7 equiv of $HAuCl_4$ per triazole, diameter = 6.8 (±0.7) nm; (E) dendrimer **5** + 10 equiv of $HAuCl_4$ per triazole, diameter = 11.0 (±1) nm; (F) dendrimer **2** + 20 equiv of $HAuCl_4$ per triazole, diameter = 11.3 (±1) nm; (G) HRTEM of dendrimer **5** + 7 equiv of $HAuCl_4$ per triazole.

was completed in 3.5 h, whereas that with the dendrimer **5** was completed in one day in order to achieve complete reduction (Figure 8).

For all the experiments, the UV−vis spectrum shows a plasmon band between 530 and 570 nm depending on the cases (see the examples with the dendrimers **9**, **10** and **11** in Figure 9). This means that all the observed AuNPs have a diameter larger than 3 nm. The transmission electron microscopy (TEM) data confirm this trend (see ESI), showing that the dendrimer **9**-stabilized AuNPs have a diameter of 23 ± 0.5 nm, the dendrimer **10**-stabilized AuNPs have a diameter of 34 ± 1 nm and the dendrimer **11**-stabilized AuNPs have a diameter of 36 ± 0.5 nm.

The various generations of "click" dendrimers **4**, **5** and **6** give the same AuNP diameters as dendrimers **9**, **10** and **11**. Indeed, the dendrimer **4**-stabilized AuNPs have a diameter of 22 ± 0.5 nm, the dendrimer **5**-stabilized AuNPs have a diameter of 33 ± 0.5 nm, and the dendrimer **3**-stabilized AuNPs have a diameter of 36 ± 1 nm (see ESI). This leads to a characteristic size for each generation of dendrimers containing or not triazole groups, and in these syntheses only the reaction time changes.

The sizes of these AuNPs are much larger than those observed with the first protocol with $NaBH_4$ in methanol. The presence of Percec-type PEG tethers in these dendrimers is required for the reduction and the stabilization of AuNPs in water.

Several tests were performed with the two PEGylated Percec-type dendrons **3** and **8** (used to synthesize the PEGylated dendrimers), and the PEG polymer **15** (mass molar: 5000 g $mol^{-1}$) (Chart 2). Mixing **3**, **8** or **15** with $HAuCl_4$ in water did not result in any color change of the yellow aqueous solution after several days nor any change in the UV−vis spectrum. Thus, reduction of AuNPs did not proceed in these cases, in sharp contrast to what was observed with the PEGylated dendrimers under the same conditions. This shows that a PEGylated dendron or PEG polymer is not sufficient to reduce $HAuCl_4$ in water, but that the PEGylated dendron must be embedded within the dendritic structure to become efficient for this process.

To further examine the frontier of the feasibility of $HAuCl_4$ reduction and AuNP stabilization in water in the absence of external reductant, we synthesized the dendrimer **16** by "click" reaction between the 27-azido dendrimer precursor of **5** and

***Chart 1.*** Structure of the Known Dendrimers **12**−**14** that Do Not Contain PEG Termini and Stabilize PdNPs[12a] but Not AuNPs.

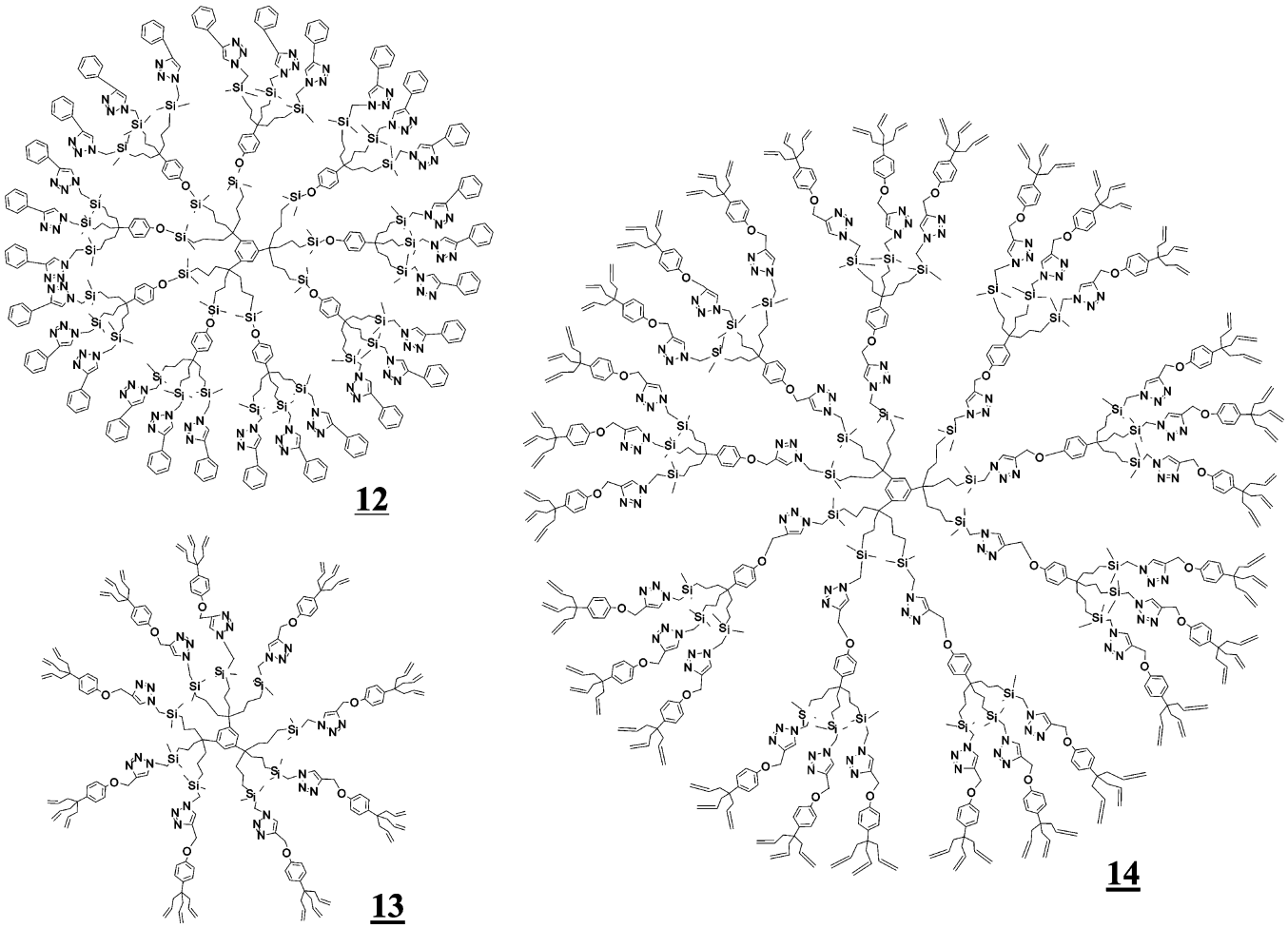
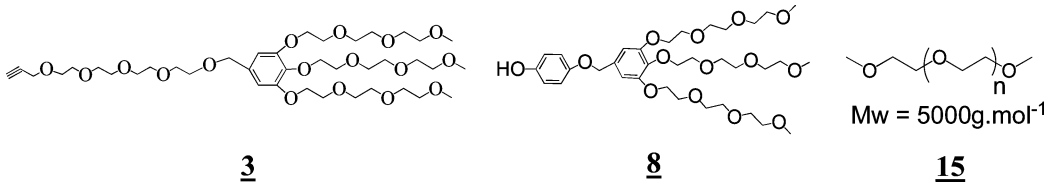



***Chart 2.*** PEG Dendrons and Polymer that Do Not Undergo AuNP Formation from $HAuCl_4$ in Water in the Absence of External Reductant, Unlike the PEGylated Dendrimers **4**−**6** and **9**−**11**

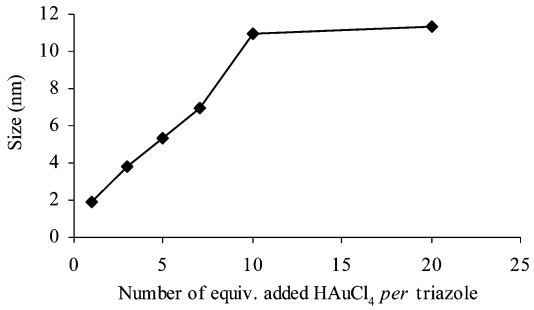



propargyltetraethylene glycol (instead of the dendron **3** used for the synthesis of **6**; compare Chart 3 with Scheme 2). The structure of **16** is thus intermediate between those of the PEGylated dendrimers **4** and **5**, but with 27 linear (nondendronic) tetraethyleneglycol tethers instead of PEGylated Percec-type dendrons (Chart 3). In **16**, the branching point of the 1 → 3 connectivity is remote from the tetraethyleneglycol groups, unlike in **4** and **5**.

Mixing this white crystalline dendrimer **16** with the yellow aqueous solution of $HAuCl_4$ resulted in a clear yellow solution from which a pale yellow precipitate formed after 15 min, whereas the solution became colorless. Addition of dichloromethane and shaking the two phases recovered the clear yellow aqueous solution of $Au^{III}$ and the colorless organic phase from which the dendrimer **16** was recovered quantitatively and identified by $^1H$ NMR. Extraction with dichloromethane apparently breaks the weak triazole−$Au^{III}$ bond, but no AuNPs were formed in this process. This experiment is in sharp contrast with the similar experiments carried with all the dendrimers terminated by Percec-type PEG dendrons that produced red AuNPs (Scheme 3).

Many transition-metal-1,2,3-triazole complexes are known with a variety of coordination modes.[11d,21] With ferrocenyl "click" dendrons and ferrocenyl-terminated "click" dendrimers related to **12**−**14**, such intradendritic triazole complexation by late transition-metal cations has also been shown by electrochemistry[11a] and X-ray crystal structures.[11d] In the present case, complexation of the triazole group of the dendrimer **4** has been monitored by UV−vis spectroscopy before $NaBH_4$ reduction to AuNPs (ESI), although the complexation mode is still unknown, the possibilities being multifold in the literature.[11d,21]

It can be concluded that the driving force provided by the linear TEG termini in **16** or by the open PEG structures **3**, **8** and **15** of Chart 1 is insufficient to reduce $Au^{III}$. This shows that it is the semicavitand-shaped Percec-type PEG, when it is sterically constrained within the dendrimer frame, that is




| equiv. number of $HAu^{III}Cl_4$ *per* triazole | AuNP diameter (nm) |
|---|---|
| 1 | 1.9 (± 0.2) |
| 3 | 3.8 (± 0.4) |
| 5 | 5.3 (± 0.5) |
| 7 | 6.8 (± 0.7) |
| 10 | 11.0 (± 1) |
| 20 | 11.3 (± 1) |

***Figure 7.*** Size variation of AuNPs stabilized by the "click" dendrimer **6** G1−81-PEG in methanol upon reduction using $NaBH_4$ in methanol.

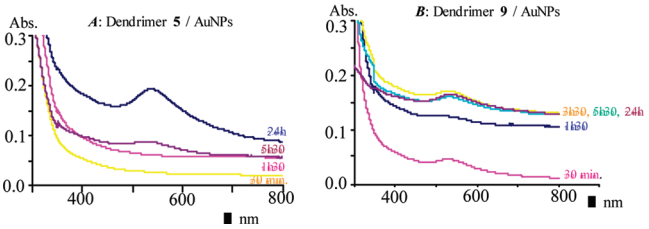



***Figure 8.*** UV−Vis spectra of AuNPs formed and stabilized by the dendrimers **5** and **9** at different times.

responsible for reduction of $HAuCl_4$ and stabilization of AuNPs. The experiment with the nonclick PEGylated dendrimers **9**-**11** that also reduce $HAuCl_4$ shows that the triazole ring is not involved in the reduction, as also confirmed by the negative result obtained with the dendrimer **16**. When both the triazole and dendronic Percec-type PEG are present in the dendrimer structure, reduction of $HAuCl_4$ still occurs, but more slowly than in the absence of triazole, because of triazole complexation. Some PEGs are known to complex and reduce $Au^{III}$ to AuNPs,[23] the mechanism involving oxidative cleavage of ether C−O bonds by the strong oxidant $Au^{III}$.[23f] It appears here that the dendronic nature of the Percec-type TEGs strongly favors this process compared to linear tetraethylene glycol termini. Chelating or encapsulating oxygen atoms of crown ethers are much more easily protonated than linear PEG,[23c] and ion pair formation den-$PEGH^+$, $AuCl_4^-$ or den-$PEGH^+$, $[AuCl_3(OH]^-$ becomes possible,[23c] which accounts for intradendritic extraction of $HAuCl_4$ by the dendritic Percec-type PEG from the peripheral aqueous medium. Finally, coordination/chelation of $Au^{III}$ by PEG oxygen atoms of the Percec-type dendron constrained in the dendrimers presumably occurs, before oxidative C−O cleavage concomitant with $Au^{III}$ reduction.

**7. AuNPs Size Variation in Water upon Change of the $AuCl_4$ Stoichiometry.** The AuNP size variation when $HAuCl_4$ is reduced and the AuNPs stabilized by dendrimers **9**, **10** and **11** in water is observed when the number of equivalents of added $HAuCl_4$ is multiplied by two and by five (i.e., 18 and 45 equiv of Au for **9**, 54 and 135 equiv of Au for **10**, and 162 and 405 equiv of Au for **11**). The TEM images were recorded (see ESI), and the diameters of the AuNPs obtained were estimated (Table 1). The diameter of dendrimer **9**-stabilized AuNPs varies from 23 ± 0.5 nm to 32 ± 1 nm, from 34 ± 1 nm to 38 ± 1 nm for dendrimer **10**-stabilized AuNPs and from 36 ± 0.5 nm to 42 ± 1 nm for dendrimer **11**-stabilized AuNPs.

**8. AuNP Formation in Methanol upon $HAuCl_4$ Reduction by Organometallic "Electron-Reservoir" Complexes.** The AuNP precursor $HAuCl_4$ was also reduced in methanol to AuNPs by the organometallic electron-reservoir sandwich complexes, $[Fe^ICp(\eta^6\text{-}C_6Me_6)]$,[24] ferrocene, ethynylferrocene and decamethylferrocene that are single-electron reductants with various redox potentials. In these cases, the AuNPs were synthesized by reaction between the "click" dendrimer **5** and a stoichiometric amount of $HAuCl_4$ *per* dendrimer triazole group, followed by reduction in methanol using the organometallic compound. The TEM data (see ESI) show that the dendrimer **5**-stabilized AuNPs obtained using the organometallic compounds are much larger than the AuNPs obtained by reduction using $NaBH_4$ (1.9 ± 0.4 nm). Indeed, the AuNP diameter synthesized using ferrocene is 38 ± 3 nm, with ethynylferrocene it is 30 ± 3 nm, with decamethylferrocene it is 23 ± 2 nm, and with $[Fe^ICp(\eta^6\text{-}C_6Me_6)]$ it is 7 ± 1 nm. The high resolution TEM (Figure 10B) shows the cubic crystalline structure of the AuNPs obtained AuNP under these conditions using $[Fe^ICp(\eta^6\text{-}C_6Me_6)]$ as the reductant.

## Discussion

Dendrimers that contain both triazole rings and TEGylated Percec-type dendrons are able to stabilize AuNPs in methanol, but related dendrimers lacking one of these structural features cannot stabilize AuNPs upon $NaBH_4$ reduction of $HAuCl_4$ in this solvent. We already know from previous electrochemical[11a] and X-ray structural studies[11d] that various late transition-metal ions are coordinated by the intradendritic triazole ligands of "click" dendrimers. Thus, in the present case, the triazole ligands analogously serve to trap the $Au^{III}$ ions inside the "click" dendrimers, then stabilization of the reduced Au atoms in AuNPs is provided by the nearby semicavitand formed by the TEGy-

(23) (a) Liu, K. J. *Macromolecules* **1968**, *1*, 308–311. (b) Yanagida, S.; Takahashi, K.; Okahara, M. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1386–1390. (c) Warshawsky, A.; Kalir, R.; Deshe, A.; Berkovitz, H.; Patchornik, A. *J. Am. Chem. Soc.* **1979**, *101*, 4249–4256. (d) Yokota, K.; Matsumura, M.; Yamaguchi, K.; Takada, Y. *Makromol. Chem. Rapid Commun.* **1983**, *4*, 721–724. (e) Adams, M. D.; Wade, P. W.; Hancock, R. D. *Talanta* **1990**, *37*, 875–883. (f) Longenberger, L.; Mills, G. *J. Phys. Chem.* **1995**, *99*, 475–478. Mathur, A. M.; Scranton, A. B. *Sep. Sci. Technol.* **1995**, *30*, 1071–1086. (g) Sanai, Y.; Ono, K.; Hidaka, T.; Takagi, M.; Cattrall, R. W. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 1165–1169. (h) Elliott, B. J.; Scranton, A. B.; Cameron, J. H.; Bowman, C. N. *Chem. Mater.* **2000**, *12*, 633–642. (i) Sakai, T.; Alexandridis, P. *J. Phys. Chem. B* **2005**, *109*, 7766–7777.

(24) (a) Hamon, J.-R.; Astruc, D.; Michaud, P. *J. Am. Chem. Soc.* **1981**, *103*, 758–766. (b) Green, J. C.; Kelly, M. R.; Payne, M. P.; Seddon, E. A.; Astruc, D.; Hamon, J.-R.; Michaud, P. *Organometallics* **1983**, *2*, 211–218. (c) Desbois, M.-H.; Astruc, D.; Guillin, J.; Varret, F.; Trautwein, A. X.; Villeneuve, G. *J. Am. Chem. Soc.* **1989**, *111*, 5800–5809.

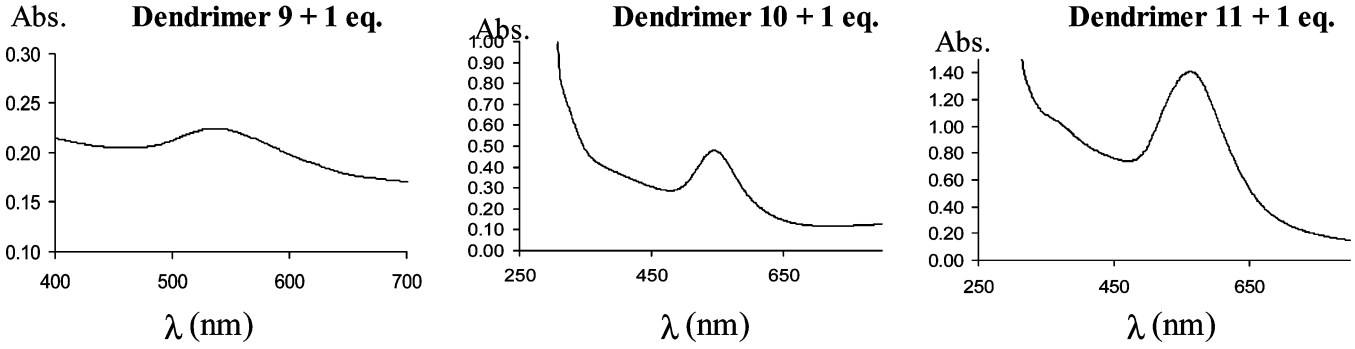
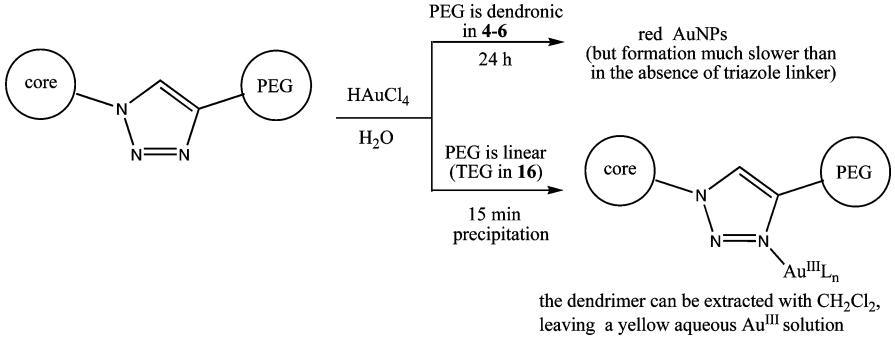



***Figure 9.*** UV−Vis spectra of AuNPs formed and stabilized by the dendrimers **9**, **10** and **11**.

***Scheme 3.*** Dramatic Influence of the Dendronic Percec-type PEG in **4**−**6** on $Au^{III}$ Reduction and AuNP Formation in Water without Additional Reductant, Compared to a Linear TEG in **16**




lated Percec-type dendrons. "Click" TEG-terminated dendrimer stabilized AuNPs formed upon $NaBH_4$ reduction in methanol, but the generation dependence influenced the AuNP size and mode of stabilization. DSAuNPs are formed with $G_0$-27TEG, and they are larger (4.1 nm) than the dendrimer and thus surrounded by several dendrimers (Figure 11). On the other hand, DEAuNPs are formed from the large $G_1$-81TEG and $G_2$-243 TEG dendrimers. These findings were obtained using a 1:1 $HAuCl_4$/triazole stoichiometry, but the AuNP size was steadily increased when this stoichiometry was increased until a plateau was reached at a 10:1 stoichiometry with $G_1$-81TEG, indicating that the AuNPs have become so large that they could no longer be encapsulated. This shows the progressive transition between DEAuNPs and DSAuNPs as well as the maximum size of AuNPs that can be reached by this method.

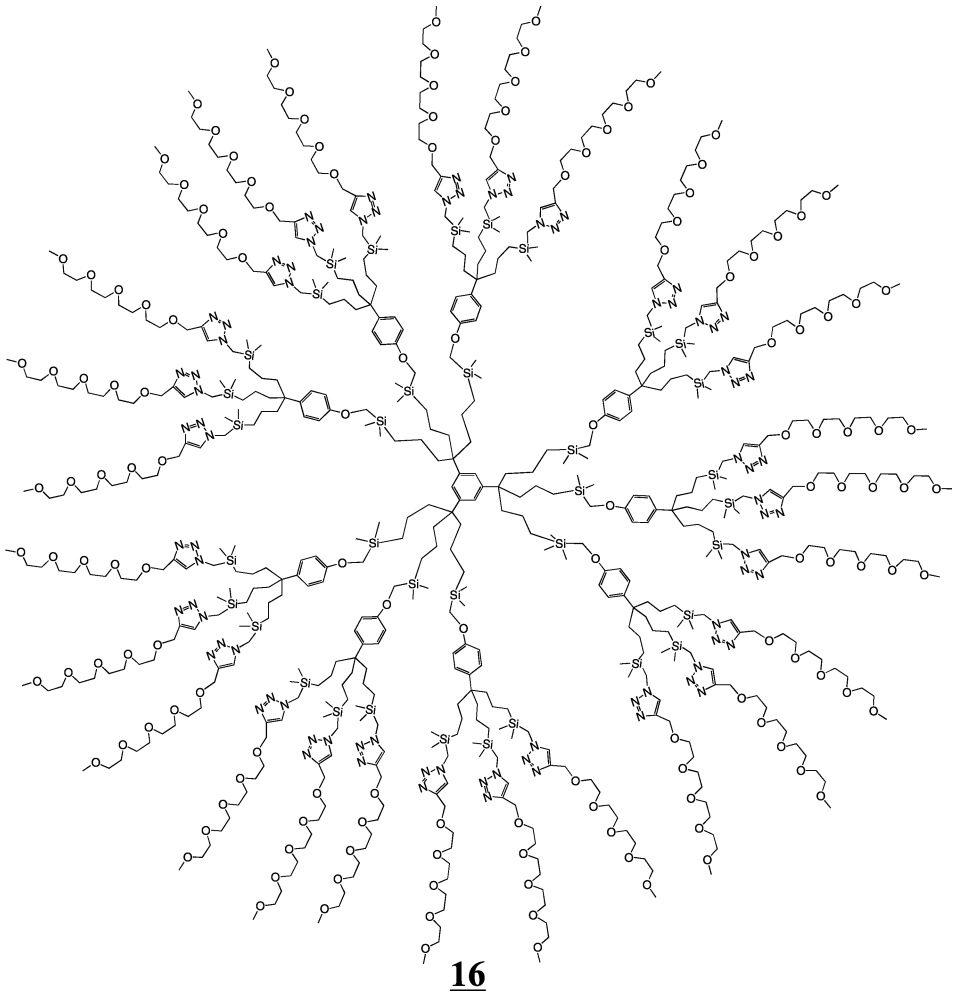
Whereas AuNPs were easily formed from PAMAM and PIP dendrimers by the pioneers in the area,[6] it is surprising that AuNPs could not be formed here by $NaBH_4$ reduction in methanol of $Au^{III}$ complexes of arene-cored "clicked" dendrimers in the absence of TEG termini. This is all the more striking as our previous studies had shown that, using these same dendrimers, PdNPs were formed and were shown to be very active in the catalysis of alkene hydrogenation and C−C forming reactions. This contrast might be due to the difference of aggregation mechanism and rate between these two metals.

Also remarkable is the success to form these AuNPs when the TEG termini were introduced as structural complement for all the dendrimers studied here. It is thus likely that this outstanding property of Percec-type TEG termini could be extended to many other dendrimers. Another interesting distinction is the impossibility to form the dendrimer-stabilized AuNPs by $NaBH_4$ reduction of $HAuCl_4$ in methanol when the arene-cored TEG-terminated dendrimers do not contain the 1,2,3-triazole ring whatever the generation (nonclick dendrimer series **9**, **10** and **11**). $NaBH_4$ is currently believed to be a convenient reductant of $Au^{III}$ to form AuNPs (despite the undesired formation of borides at the AuNP surface),[24b] but this study demonstrates that it does not always work, probably because in this precise case the reduction is too fast to be compatible with stabilization of the AuNPs.

Even if $NaBH_4$ fails to lead to the formation of AuNPs with TEG-terminated dendrimers that do not contain a triazole ring, however, the presence of Percec-type TEG termini is sufficient to allow the formation of the AuNPs in water in this case in the absence of reductant. The dendritic effect is required for this property, as it is shown that nondendritic linear PEGs, tripodal dendronic PEGs that are not incorporated in dendrimers, and even a "click" dendrimer terminated by 27 linear (non dendronic) TEG tethers does not have this property. $Au^{III}$ is a rather strong oxidant,[25] but oxidation of nondendritic PEG is endergonic and not sufficiently entropy-driven. On the other hand, $Au^{III}$ encapsulation achieved upon multiple proton coordination by the oxygen atoms of the TEG semicavitands is facilitated by the dendritic constraint, which brings about ion pairing to trap $Au^{III}$ with favorable entropy conditions for $Au^{III}$ reduction. Yet, the AuNP formation is slow in "click" dendrimers terminated by Percec-type PEG dendrons, due to the $Au^{III}$-triazole coordination that is distal from the dendronic PEG reduction site. Either the requirement of a distal electron transfer slows it down or the reversible $Au^{III}$-triazole coordination renders $Au^{III}$ less available at the dendronic PEG reduction site.

(25) Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th ed.; John Wiley: New York,; pp 1084−1086.

***Chart 3.*** Structure of the Dendrimer **16** that Contain Linear (non-Percec-type) TEG Termini and Does Not Undergo AuNP Formation from $HAuCl_4$ in Water in the Absence of External Reductant



**16**

***Table 1.*** Size Evolution of AuNPs Stabilized by Dendrimers **9**, **10** or **11** in Water

| dendrimer + number of equiv of Au per dendron | AuNP diameter (nm) |
|---|---|
| Dendrimer **9** + 1 equiv | 23 ± 0.5 |
| Dendrimer **9** + 2 equiv | 26 ± 1.0 |
| Dendrimer **9** + 5 equiv | 32 ± 1.0 |
| Dendrimer **10** + 1 equiv | 34 ± 1.0 |
| Dendrimer **10** + 2 equiv | 36 ± 0.5 |
| Dendrimer **10** + 5 equiv | 38 ± 1.0 |
| Dendrimer **11** + 1 equiv | 36 ± 0.5 |
| Dendrimer **11** + 2 equiv | 38 ± 1.0 |
| Dendrimer **11** + 5 equiv | 42 ± 1.0 |

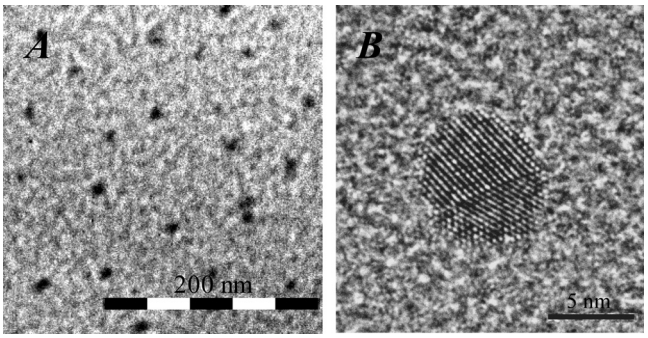



***Figure 10.*** (A) TEM of the dendrimer **5** + 1 equiv of $HAuCl_4$ reduced by $[Fe^{I}Cp(\eta^6\text{-}C_6Me_6)]$. (B) HRTEM of the dendrimer **5** + 1 equiv of $HAuCl_4$ reduced by $[Fe^{I}Cp(\eta^6\text{-}C_6Me_6)]$.

The large size of the AuNPs formed by this process is due to this very slow kinetics. This means that the AuNPs start growing inside the dendrimers, and that these germs continue growing outside the dendrimers owing to their large size by trapping the Au atoms formed in the TEG semicavitands near the dendrimer periphery. It is likely that, once the large AuNPs grow, the native Au atoms do not form small stable DEAuNPs inside the dendrimer, because the latter are not observed by TEM.

Note that the AuNPs obtained by this method have the same size whether or not they contain triazole ligands, confirming that it is the TEG oxygen pseudocavities that play the main role in the AuNP formation in this case rather that the triazole ring. The DSAuNPs formed in this way are much larger than those formed by $NaBH_4$ reduction, because the driving force is considerably larger with $NaBH_4$ than with the TEG semicavitand dendrimer termini.

It is surprising that, owing to the undesired boride impurities formed at the AuNP surface of AuNPs synthesized using $NaBH_4$,[18d] no monoelectronic reductant has been probed to form clean AuNPs. For biomedical applications, the AuNPs are usually synthesized with the Turkevich method,[26] because most (although not all) of the temporary citrate stabilizers can be removed to introduce the biomedical probe or target, and the large AuNPs formed by this method allow monitoring an intense

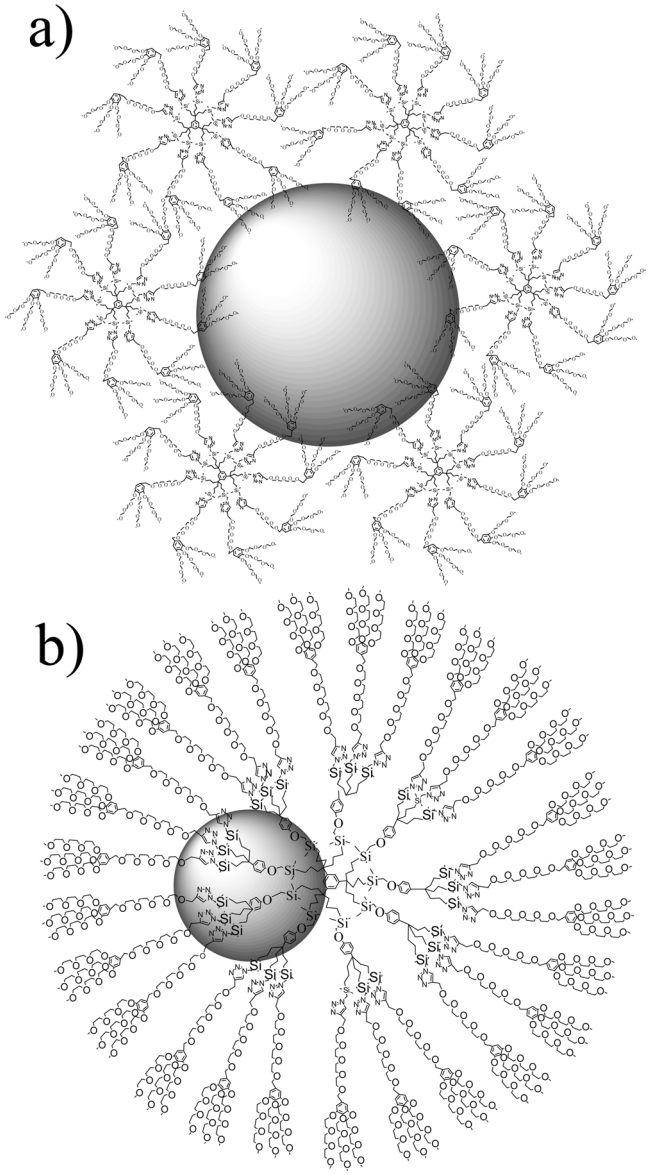



***Figure 11.*** (a) AuNPs stabilized by several dendrimers **4**; (b) dendrimer **5**-encapsulated AuNPs.

plasmon absorption. Also, whereas small AuNPs (< 5 nm) are of great interest for efficient catalysis,[27] large AuNPs are important in nanomedicine, because the plasmon band (AuNP > 3 nm) is an indispensable tool in this later area.[18]

In the present study, the use of single-electron reductants successfully leads to the formation of AuNPs that are much larger than those formed using $NaBH_4$ reduction. This is due to the fact that the mechanism of $NaBH_4$ reduction follows inner-sphere electron transfer involving chloride elimination from $AuCl_4^-$, whereas the mechanism of the single-electron reductants involves outer-sphere electron transfer. As shown by the seminal work of Henry Taube, inner-sphere mechanisms are considerably superior to outer-sphere electron-transfer mechanisms in terms of reaction kinetics.[28] Again, slow reduction is well-known to result in a prolonged aggregation process leading to large NPs.[26] Reetz has shown a linear correlation between the driving force of carboxylate reductants and the PdNP size, that is, the PdNPs are all the larger as the driving force is weaker.[29] This is also what is found here with the series of monoelectronic reductants, as the DSAuNPs formed are all the larger as the standard oxidation potential of the reductant is more positive (or less negative). Since the reactions of electron-reservoir complexes are clean because, by definition, both the oxidized and reduced forms are stable,[24] it is possible to define the size of the DSAuNPs between 7 nm (strong $Fe^I$ monoelectronic reductant) and 38 nm (weakest $Fe^{II}$ monoelectronic reductant). The standard potentials of these electron-reservoir complexes are perfectly defined and can be easily tuned even with small variations by change of the nature and number of ring substituents of the transition-metal sandwich complex.[30] This flexibility allows to also finely tune the AuNPs size without inhibiting the AuNP surface upon ligand coordination.

## Concluding Remarks

This study shows the critical structural conditions for the dendrimer-induced formation of DEAuNPs and DSAuNPs of various sizes ranging from 1.8 to 42 nm. A variety of new dendrimers synthesized using 1 → 3 connectivity with Percec-type TEG termini provide ideal conditions for AuNP formations from $HAuCl_4$ either using $NaBH_4$ as the reductant or without external reductant. With $NaBH_4$, it is also indispensable to use "click" dendrimers terminated by Percec-type TEG dendrons in order to introduce $Au^{III}$ inside the dendrimer by coordination to the triazole rings, which adequately modulates the nucleation. On the other hand, in the absence of external reductant, $Au^{III}$-triazole coordination slows down $Au^{III}$ reduction, because the distal Percec-type dendron itself is the reductant. The semicavitand effect is then crucial, as shown by the failure of $Au^{III}$ reduction using a "click" dendrimer terminated by a linear tertraethylene glycol instead of a Percec-type TEG dendron. DSAuNPs are formed with all the dendrimers from $HAuCl_4$ in this way in the absence of additional reductant (23 to 42 nm-size depending on the generation but not on presence of triazole in the dendrimer structure). Finally, choosing the $AuCl_4$/dendrimer stoichiometry can orient the size of the AuNPs formed in these processes. Monoelectronic reductants have also been used for the first time for the reduction of $HAuCl_4$ to AuNPs. Their outer-sphere reduction mechanism implies a much slower reduction than with the inner-sphere reductant $NaBH_4$, and the size of the DSAuNP formed (between 7 and 38 nm) is directly related to the standard oxidation potentials of the $Fe^I$ and $Fe^{II}$ reductants. This provides the possibility to finely tune the DSAuNP size.

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All these water-soluble dendrimer-stabilized PEGylated AuNPs are only weakly stabilized and thus should be very useful for catalytic (small size) and biomedical applications (large size).

## Experimental Section

**1. Synthesis and Characterization of the Alkyne Dendron 3 (see ESI).** A Percec-type dendron[19] containing a tris-(triethylene glycol) group (1 g, 1.57 mmol) and tetraethylene glycol (2.95 g, 15.7 mmol) were introduced into a Schlenk flask, and dry THF (50 mL) was added. NaH (108 mg, 2.7 mmol) was added to the solution. The mixture was stirred for 12 h at 50 °C. At the end of the reaction, water was added, and then THF was removed under vacuum. The product was extracted with $CH_2Cl_2$ and purified by chromatography (MeOH) giving 1 g of yellow oil (83% yield).

The tris-(triethylene glycol) tetraethylene glycol dendron (600 mg, 0.65 mmol) and dry THF (50 mL) were introduced into a Schlenk flask, and NaH (47 mg, 1.95 mmol) was added at 0 °C. Propargyl bromide (155 mg, 1.3 mmol) was added to the solution, and the mixture was stirred for 2 h at 0 °C, then 2 h at 25 °C. At the end of the reaction, water was added, then THF and excess propargyl bromide were removed under vacuum. The product was extracted with $CH_2Cl_2$, yielding 600 mg of yellow oil (95% yield). $^1$H NMR ($CDCl_3$, 250 MHz): 6.39 (2H, C*H*-arom. extern), 4.26 (2H, O−C*H*$_2$-arom. extern), 3.98 (4H, C*H*$_2$O-arom. extern and C*H*$_2$-alkyne), 3.46 (30H, OC*H*$_2$C*H*$_2$O), 3.17 (9H, C*H*$_3$O), 2.36 (1H, C−C*H* alkyne); $^{13}$C NMR ($CDCl_3$, 62 MHz): 152.41 (*C*q-O arom.), 137.50 (*C*q-$CH_2$ arom.), 133.63 (Cq-*C*H2−O), 106.87 (*C*H arom.), 79.54 (*C*q alkyne), 74.75 (*C*H alkyne), 70.46 (O-*C*H$_2$), 58.74(O-*C*H$_3$), 58.13 (*C*H$_2$-alkyne). Infrared $\upsilon_{alkyne}$: 2100 cm$^{-1}$; MALDI TOF: Calcd for $C_{39}H_{68}O_{17}$: 808; found: 831 ($MNa^+$)

**2. General Procedure for the Synthesis of the "Clicked" PEG Dendrimers 4, 5 and 6.** The azido-terminated dendrimer (**2** for the synthesis of the dendrimer **5**, 1 equiv.) and the alkyne dendron **3** (1.5 equiv. *per* branch) were dissolved in THF. At 0 °C, $CuSO_4$ was added (2 equiv per branch, 1 M water solution), followed by the dropwise addition of a freshly prepared solution of sodium ascorbate (4 equiv per branch, 1 M water solution) in order to set a 1:1 (THF/water) ratio. The solution was allowed to stir for 12 h at 25 °C under $N_2$. After removing THF under vacuum, $CH_2Cl_2$ and an aqueous ammonia solution were added. The mixture was allowed to stir for 10 min to remove all the $Cu^{II}$ trapped inside the dendrimer as $[Cu(NH_3)_6]^{2+}$. The organic phase was washed twice with water, dried with sodium sulfate, and the solvent was removed under vacuum. The product was precipitated with MeOH/ether in order to remove the excess dendron.[19] Yields: 96% (**4**); 95% (**5**) and 92% (**6**). (See details in the ESI.)

Characterization of **4**: $^1$H NMR ($CDCl_3$, 250 MHz): 7.45 (9H, C*H*-triazole), 6.93 (36H, C*H*-arom. intern), 6.56 (18H, C*H*-arom. extern), 4.62 (18H, triazole-C*H*$_2$-0), 4.43 (18H, O−C*H*$_2$-arom. extern), 4.11 (72H, C*H*$_2$O-arom. extern and Si−C*H*$_2$-triazole), 3.64 (414H, OC*H*$_2$C*H*$_2$O), 3.37 (27H, C*H*$_3$O), 1.59 (18H, C*H*$_2$-CH$_2$CH$_2$Si), 1.07 (18H, CH$_2$C*H*$_2$CH$_2$Si), 0.60 (18H, CH$_2$CH$_2$-C*H*$_2$Si), 0.006 (54H, Si(C*H*$_3$)$_2$); $^{13}$C NMR ($CDCl_3$, 62 MHz): 151.62 (*C*H, extern arom.), 144.48 ($C_q$ of triazole), 136.83 (*C*q, arom. core), 132.75 (*C*q, arom. extern), 123.52 (*C*H of triazole and arom. core), 106.23 ($C_q$CH$_2$O), 69.54 (OCH$_2$CH$_2$O), 63.53 (triazole-*C*H$_2$−O), 58.00 (*C*H$_3$O), 53.38 (OCH2-arom. extern), 43.77 (*C*H$_2$CH$_2$CH$_2$Si), 42.7 (SiC*H*$_2$-triazole), 40.93 (*C*q-arom. intern), 17.82 (CH$_2$*C*H$_2$CH$_2$Si), 14.90 (CH$_2$CH$_2$*C*H$_2$Si), −4.84 (Si(*C*H$_3$)$_2$); DOSY: $D = 1.16\ (\pm 0.1) \times 10^{-10}$ m$^2$/s, Rh = 4.9 (±0.1) nm (D: diffusion coefficient; Rh: hydrodynamic radius); IR: no alkyne and azide bands; MALDI-TOF mass spectrum: Calcd for $C_{414}H_{741}O_{153}N_{27}Si_9$: 8798; found: 8824 ($MNa^+$). Anal. Calcd for $C_{414}H_{741}O_{153}N_{27}Si_9$: C 56.52, H 8.49; found: C 56.31, H 8.49; light scattering: diameter = 9 ± 0.8 nm.

**3. Synthesis and Characterization of the Phenol Dendron 8 (see ESI).** The tris-(triethylene glycol) dendron (300 mg, 0.46 mmol) and hydroquinone (251 mg, 2.28 mmol) were introduced into a Schlenk flask, and dry DMF (30 mL) was added. $K_2CO_3$ (315 mg, 2.28 mmol) was added to the solution. The mixture was stirred for 18 h at 80 °C under reflux. At the end of the reaction, DMF was removed. The product was extracted with $CH_2Cl_2$, washed with water, and purified by chromatography ($CH_2Cl_2$/MeOH, (97:3). 205 mg of a yellow oil was obtained (65% yield). $^1$H RMN ($CDCl_3$, 250 MHz): 3.35 (C*H*$_3$O); 3.63 (C*H*$_2$O); 4.11 (C*H*$_2$O arom.); 4.83 (OC*H*$_2$arom.); 6.59 (C*H* arom.); 6.87 (C*H* arom.−OH); $^{13}$C NMR ($CDCl_3$, 62 MHz): 152.82 (*C*q-O−CH$_2$), 152.19 ((Cq−OH),150.56 (*C*q extern.-CH$_2$−O), 137.87 (*C*q middle-CH$_2$−O), 132.83 (*C*H$_2$−Cq), 116.17 (*C*H arom.-Cq-O), 107.19 (*C*H arom.-Cq-CH$_2$), 71.93 (O−CH$_2$-arom), 70.71 (O-*C*H$_2$), 59.06 (O-*C*H$_3$). MALDI TOF: Calcd for $C_{34}H_{54}O_{14}$: 686.35; found: 709.34 ($MNa^+$). Anal. Calcd for $C_{54}H_{54}O_{14}$: C 59.46, H 7.92; found: C 59.21, H 8.18.

**4. General Procedure for the Synthesis of the Dendrimers 9, 10, and 11 by the Williamson Reaction.** The iodo-terminated dendrimer[20]d **7** ($5.46 \times 10^{-6}$ mol) and the phenol dendron **8** (10 equiv for $G_0$, 30 equiv for $G_1$ and 90 equiv for $G_2$) were introduced into a Schlenk flask, and dry DMF (30 mL) was added, then $K_2CO_3$ (2 equiv per dendron) was added to the solution. The mixture was stirred for 2 days at 80 °C under reflux. At the end of the reaction, DMF was removed. The product was extracted with $CH_2Cl_2$ and washed with water. $G_0$ and $G_1$ were purified by chromatography ($CH_2Cl_2$:MeOH, (97:3) to remove the excess dendron and then (90:10) to extract the dendrimer). $G_2$dHQ was precipitated with MeOH/ether in order to remove the excess dendron. The yields were 80% for **9** ($G_0$), 78% for **10** ($G_1$) and 85% for **11** ($G_2$).

Characterization of the dendrimer **9**: $^1$H NMR ($CDCl_3$, 250 MHz): 6.92 (C*H*-arom. core), 6.87 (C*H*-arom. intern), 6.65 (C*H*-arom. extern), 4.85 (0- C*H*$_2$-arom. extern), 4.16 (C*H*$_2$O-arom. extern), 3.65 (OC*H*$_2$C*H*$_2$O and Si−C*H*$_2$O), 3.38 (C*H*$_3$O), 1.69 (C*H*$_2$CH$_2$CH$_2$Si), 1.12 (CH$_2$C*H*$_2$CH$_2$Si), 0.62 (CH$_2$CH$_2$C*H*$_2$Si), 0.06 (Si(C*H*$_3$)$_2$); $^{13}$C NMR ($CDCl_3$, 62 MHz): 156.09 (O-*C*q intern), 152.61 (*C*q intern), 144.71 (*C*q arom. Core), 137.97 (*C*q-Cq intern), 130.95 (*C*H arom. extern), 118.55 (*C*H arom. core), 115.61 (*C*H-arom intern), 114.79 (*C*H arom extern), 107.07 (*C*H arom intern), 72.3 (OCH$_2$CH$_2$), 70.80 (OCH$_2$ arom extern), 68.85 (SiCH$_2$O), 59.05 (*C*H$_3$O), 43.77 (*C*H$_2$CH$_2$CH$_2$Si), 17.82 (CH$_2$CH$_2$CH$_2$Si), 14.49 (CH$_2$CH$_2$*C*H$_2$Si), −4.58 (Si(*C*H$_3$)$_2$). MALDI TOF: Calc. for $C_{369}H_{606}O_{126}Si_9$: 7311.54; found: 7334.47 ($MNa^+$); DOSY: $D = 1.47\ (\pm 0.1) \times 10^{-10}$ m$^2$/s, Rh = 3.9 (±0.3) nm (D: diffusion coefficient; Rh: hydrodynamic radius); SEC: polydispersity = 1.05. Anal. Calcd for $C_{369}H_{606}O_{126}Si_9$: C 60.62, H 8.35; found: C 59.64, H 8.57.

**5. Synthesis and Characterization of the Dendrimer 16.** The 27 azido-terminated dendrimer precursor of **5** and **16** (see structure in ESI)[11a,12a] (0.2 g, 0.032 mmol) and tetraethylene glycol methyl propargyl ether (0.319 g, 1.296 mmol, 1.5 equiv per branch) were dissolved in 50 mL of THF. At 0 °C, $CuSO_4$ was added (0.431 g, 1.728 mmol, 2 equiv per branch, 1 M water solution), followed by dropwise addition of a freshly prepared solution of sodium ascorbate (0.685 g, 3.456 mmol, 4 equiv. *per* branch, 1 M water solution) in order to set a 1:1 (THF/water) ratio. The solution was allowed to stir for 12 h at 25 °C under $N_2$. After removing THF under vacuum, $CH_2Cl_2$ and an aqueous ammonia solution (28% w/w) were added. The mixture was allowed to stir for 10 min in order to remove all the $Cu^{II}$ trapped inside the dendrimer as $[Cu(NH_3)_6]^{2+}$. The organic phase was washed twice with water, dried with sodium sulfate, and the solvent was removed under vacuum. The product was precipitated with MeOH/ether to remove the excess of tetraethylene glycol methyl propargyl ether; 0.336 g of **16** was obtained (81% yield). $^1$H NMR ($CDCl_3$, 250 MHz): 7.40 (27H, *CH*-tiazole), 7.08 (18H, *CH*-arom. extern.), 7.02 (3H, *CH*-arom. intern.), 4.61 (54H, triazole-*CH*$_2$-O), 3.81 (18H, *CH*$_2$O-arom.), 3.49−3.62 (432H, O*CH*$_2$*CH*$_2$O), 3.33 (81H, *CH*$_3$O), 1.55 (72H, *CH*$_2$CH$_2$CH$_2$Si), 1.04 (72H, CH$_2$*CH*$_2$CH$_2$Si), 0.55 (72H, CH$_2$CH$_2$*CH*$_2$Si), 0.06 (54H, O−CH$_2$Si(*CH*$_3$)$_2$), 0.007 (162H, trazole-CH$_2$Si(*CH*$_3$)$_2$). $^{13}$C NMR ($CDCl_3$, 62 MHz): 158.96 (Cq of O-arom.), 144.53 (Cq of triazole),

138.61 (Cq, arom. core) 126.94 (*C*H-arom.) 123.26 (*C*H of triazole and arom. core), 113.36 (*C*H-arom.), 70.33 ($OCH_2CH_2O$), 69.39 (Si-$CH_2$-O), 64.51 (triazole-$CH_2$−O), 58.87 ($CH_3O$), 42.28 ($CH_2CH_2CH_2Si$), 41.7 ($SiCH_2$-triazole), 40.7 (Cq-arom. inter.), 17.26 ($CH_2CH_2CH_2Si$), 14.64 ($CH_2CH_2CH_2Si$), −4.09 ($Si(CH_3)_2$). IR: no alkyne and azide bands. MALDI TOF: Calcd for $C_{612}H_{1187}O_{144}N_{81}Si_{36}$: 12946.297; found: 12971, major peak (calcd: 12969: $MNa^+$). Anal. Calcd for $C_{612}H_{1187}O_{144}N_{81}Si_{36}$: C 56.78, H 8.85; found: C 55.68, H 8.46.

**6. General Procedure for AuNPs Reduction in Methanol with Dendrimers 4, 5 and 6.** The following procedure is described using the preparation of the dendrimer **4**: 1 mL of a $1.14 \times 10^{-4}$ M solution of dendrimer (1 mg, $1.14 \times 10^{-4}$ mmol) in MeOH was introduced into a Schlenk flask under nitrogen, then 0.349 mL of a $2.94 \times 10^{-3}$ M solution of $HAuCl_4$ (0.349 mg, $1.03 \times 10^{-3}$ mmol, 1 equiv per triazole) and 4.65 mL of MeOH was added in order to obtain a solution $2.21 \times 10^{-4}$ M (in Au). The solution was stirred for 1 h, the reductant $NaBH_4$ (0.39 mg), [$Fe^{I}Cp(\eta^6$-$C_6Me_6)$] (4.4 mg), ferrocene (1.92 mg), ethynylferrocene (2.16 mg) or decamethylferrocene (3.36 mg)] was added ($1.03 \times 10^{-2}$ mmol, 10 equiv per Au), and the yellow solution turned to golden brown indicating the formation of the AuNPs.

**7. General Procedure for the Preparation of AuNPs in Water without Reductant.** The following procedure is described using the preparation of the dendrimer **9**:1 mL of a $1.37 \times 10^{-4}$ M solution of dendrimer (1 mg, $1.37 \times 10^{-4}$ mmol) in $H_2O$ was placed into a Schlenk flask under ambient condition, then 0.416 mL of a $1.23 \times 10^{-3}$ M solution of $HAuCl_4$ (0.416 mg, $1.23 \times 10^{-3}$ mmol, 1 equiv per tether). 1.584 mL of $H_2O$ was added in order to obtain a final volume of 3 mL. The solution was stirred, and the yellow solution turned to pink then red, indicating the formation of the AuNPs.

**8. Transmission Electron Microscopy (TEM and HRTEM).** The samples were prepared by placing a drop of $1.6 \times 10^{-4}$ M solution of AuNPs (concentration in mol Au) on a holey-carbon-coated Cu TEM grid and they were then analyzed with a JEOL JEM 1011 machine.

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**Note Added after ASAP Publication.** The version published ASAP on February 4, 2010, had incorrect labeling of Figures 10 and 11. The corrected version will publish with the issue on March 3, 2010.

**Supporting Information Available:** Details of the syntheses, characterizations, $^1H$ and $^{13}C$ spectra for all the new dendrons and dendrimers, size-exclusion chromatograms of the dendrimers **9**−**11**, determination of the diffusion coefficient of the dendrimers by DOSY NMR, transmission electron microscopy of the DEAuNPs and DSAuNPs, and UV−vis spectra of $HAuCl_4$, complexation by dendrimer **4**, and reduction to AuNPs by $NaBH_4$. This material is available free of charge via the Internet at http://pubs.acs.org.

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