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# "Click" Synthesis of Nona-PEG-branched Triazole Dendrimers and Stabilization of Gold Nanoparticles That Efficiently Catalyze *p*-Nitrophenol Reduction

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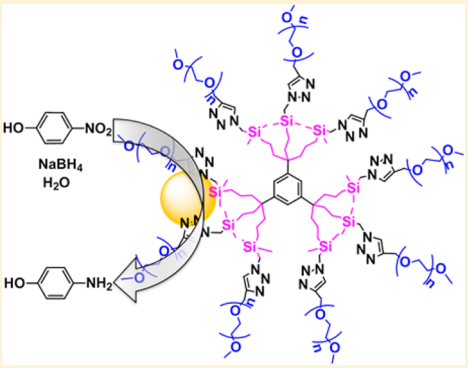
Supporting Information

**ABSTRACT:** Two new water-soluble 1,2,3-triazole-containing nona-PEG-branched dendrimers are obtained with nine intradendritic 1,2,3-triazoles (trz). Addition of $HAuCl_4$ in water to these dendrimers quantitatively leads to the intradendritic formation of $AuCl_3$(trz) moieties subsequent to complete $Cl^-$ substitution by trz on Au(III), whereas the analogous complexation reaction of $AuCl_3$ with a linear PEG trz ligand forms only an equilibrium between trz-coordinated Au(III) and Au(III) that is not coordinated to trz. Reduction of the dendrimer-Au(III) complexes to $Au^0$ by $NaBH_4$ then leads to stabilization of gold nanoparticles (AuNPs) in water. The sizes of the AuNPs stabilized by the dendritic macromolecules are further controlled between 1.8 and 12 nm upon selecting the stoichiometry of Au(III) addition per dendritic trz followed by $NaBH_4$ reduction. With a 1:1 Au/trz stoichiometry, the AuNP size depends on the length of the PEG tether of the dendrimer; small dendrimer-encapsulated AuNPs are formed with PEG2000, whereas large AuNPs are formed with PEG550. With Au/trz stoichiometries larger than unity, Au(III) is reduced outside the macromolecule, resulting in the formation of large interdendritically stabilized AuNPs. The formation of very small and only mildly stabilized AuNPs by neutral hydrophilic triazole ligands offers an opportunity for very efficient *p*-nitrophenol reduction by $NaBH_4$ in water at the AuNP surface.




## INTRODUCTION

Dendrimers that are classic synthetic macromolecules with well-defined topological flower-like structures have been demonstrated to have an extraordinary ability to hold hydrophobic guests by noncovalent bonding including physical encapsulations, van der Waals forces, hydrogen-bond interactions, and hydrophobic interactions.[1] The dendrimer−metal nanoparticle (NP) host−guest composites are synthesized through a template approach in which metal ions are entrapped in the interior of dendrimers due to the functional groups and the steric embedding effects and then reduced chemically. These dendrimer−NP composites have been modified to exhibit sufficient solubility and stability, resulting in their potential applications *inter alia* in catalysis,[2] photophysics,[3] diagnosis,[4] and sensing.[5]

Catalysis by dendrimer-encapsulated metal NPs was pioneered by Crooks' group[6] using polyamidoamine (PAMAM) dendrimers.[7] Subsequently, many reports have appeared on the stabilization of and catalysis by precious metal NPs (Pd, Pt, and Au) in various dendrimers.[8] In particular, attention has been focused on the dendrimer-stabilized AuNPs that have applications in both drug delivery and surface plasmon-based photothermal diagnosis and therapy,[9] whereas the catalytic properties of dendrimer-stabilized AuNPs were often investigated in the form of bimetal alloys or nanocomposites.[10]

"Click" dendrimers terminating with triethylene glycol (TEG) branched tris-dendrons[11] have been used for the stabilization of AuNPs subsequent to coordination of their trz ligands. It was supposed that AuNPs are either encapsulated in the dendrimers or surrounded by several dendrimers, which depends on both the size of the AuNPs and the morphology of the dendrimers.[11] It was also reported that the TEG dendron-terminated "click" dendrimer-stabilized PdNPs displayed impressive activity in the Suzuki−Miyaura reaction in aqueous medium.[12] Significantly, numerous studies in catalysis under various "green" conditions have shown that the dendrimer plays the role of the nanoreactor and nanofilter.[2]

One of our general goals is to design water-soluble and biocompatible nanomaterials in order to apply them to sensing, catalysis, and biomedicine.[13] For this purpose, PEG-terminated dendrimers fulfill these requirements and moreover provide the possibility to benefit from the enhanced permeability and retention (EPR) effect upon accumulating in tumoral tissues.[14] The association of AuNPs[15] with dendrimers is of particular interest given their multiple applications in catalysis,[16]

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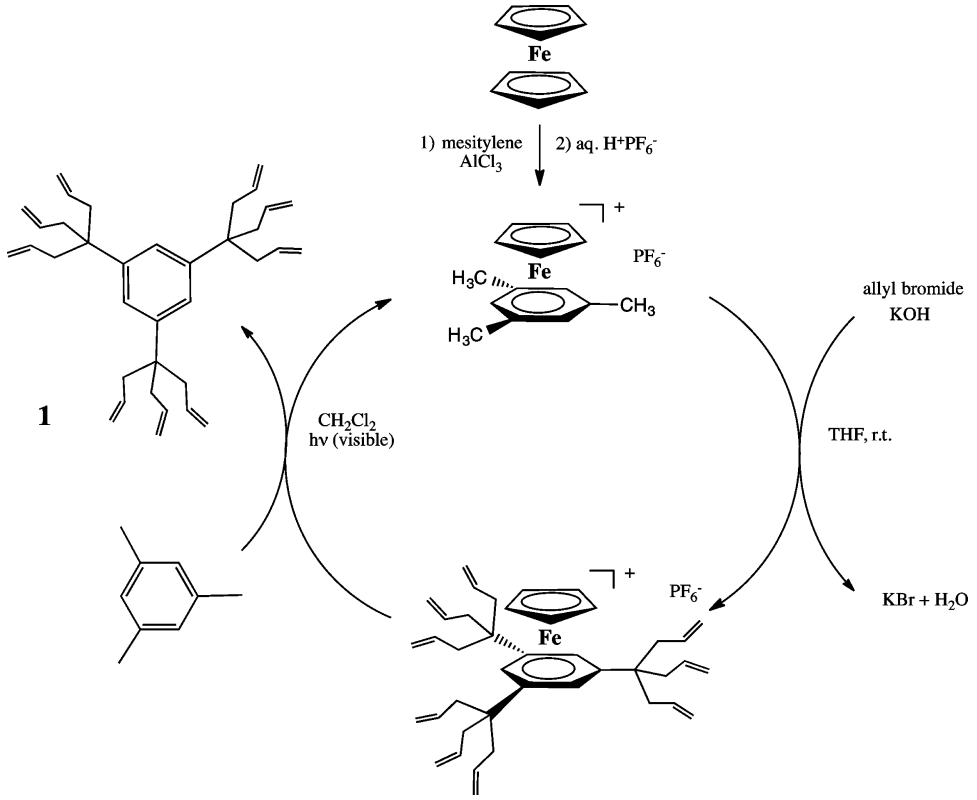
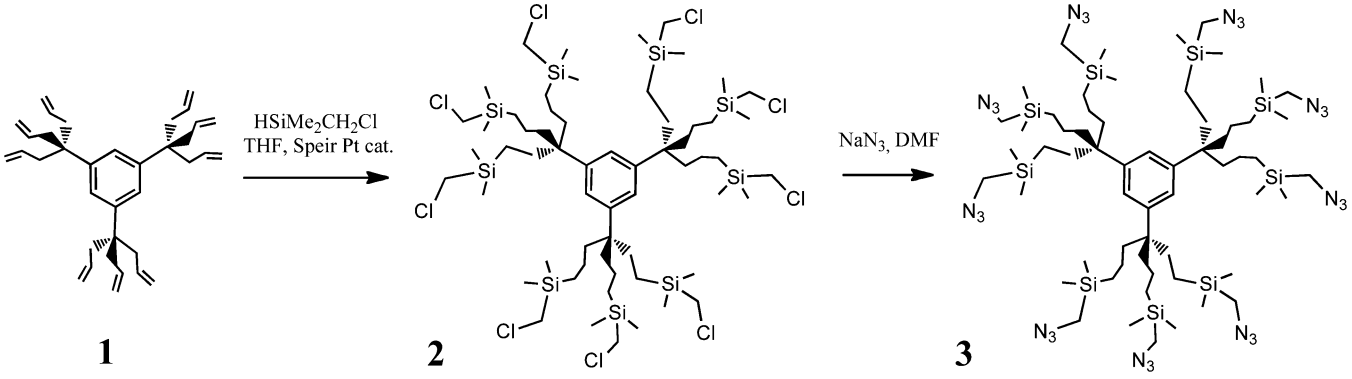
Scheme 1. $\eta^5$-$C_5H_5Fe^+$-Induced Nona-allylation of Mesitylene Yielding the Nona-allylated Core 1




Scheme 2. Synthesis of the Nona-azide 3 from the Nonaolefin Core 1 via 2




photonics,[17] and biomedicine.[18] The activation of aromatics upon temporary $\pi$ complexation by late transition metal groups,[19] in particular in the $[Fe(\eta^5\text{-}C_5H_5)(arene)]^+$ complexes,[20] provides a powerful means of functionalization and, in particular, for the synthesis of dendritic cores, dendrons, and dendrimers with 1 → 3 connectivity.[21] Thus, we have applied the $\eta^5$-$C_5H_5Fe^+$-induced polyallylation[20,22] of polymethylbenzene, in particular the nona-allylation of mesitylene giving **1** (Scheme 1),[22] for the construction of nona-PEG-terminated dendrimers.[23]

Therefore, the nona-allylated core **1** obtained as shown in Scheme 1 was hydrosilylated with dimethylchloromethylsilane, and the product **2** was submitted to nucleophilic substitution of chloride by azide via reaction with $NaN_3$ to yield **3** (Scheme 2).[23]

The known nona-azide **3** is a very practical starting material for a variety of copper-catalyzed alkyne azide cycloaddition (CuAAC) "click" reactions and was applied here in the investigation of such reactions in order to introduce PEG tethers together with triazole (trz) rings onto the dendrimers using propargyl-PEG derivatives. Herein we report these syntheses and characterizations of the 1,2,3-triazole dendrimers obtained in this way, the complexation of Au(III) to the intradendritic trz ligands upon reaction with $HAuCl_4$, and further introduction of AuNPs of catalytic interest by reduction of $Au^{III}$ using $NaBH_4$. The variation of parameters leading to these AuNP syntheses has been examined for further catalysis of *p*-nitrophenol reduction by these AuNPs that are only mildly stabilized by the trz ligands, as well as the influence of the AuNP core size on the catalytic reduction rate.

## RESULTS AND DISCUSSION

**Synthesis of Dendrimers.** As a versatile substrate, the known arene-cored, nonabranched dendrimer with azido termini **3** was synthesized according to Schemes 1 and 2.[11] Synthesis of PEG-branched nonadendrimers was then con-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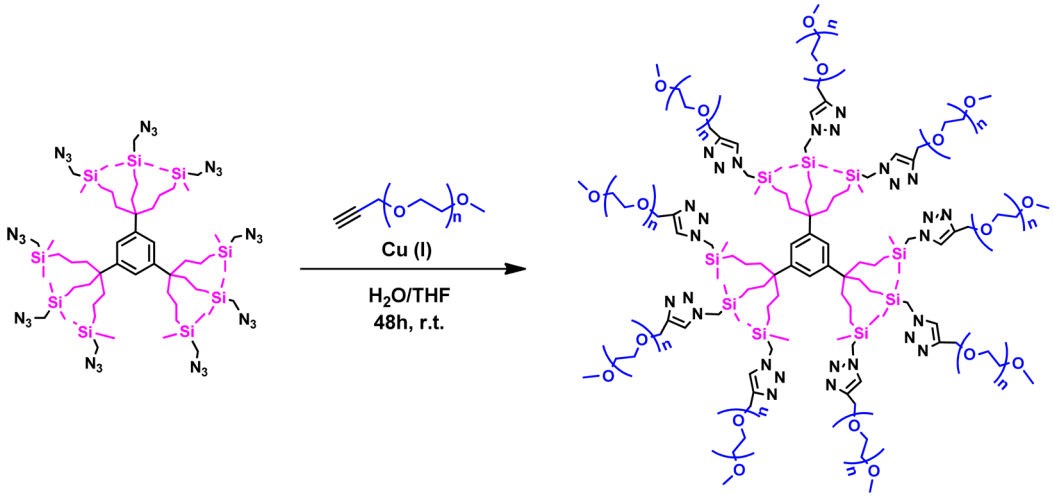
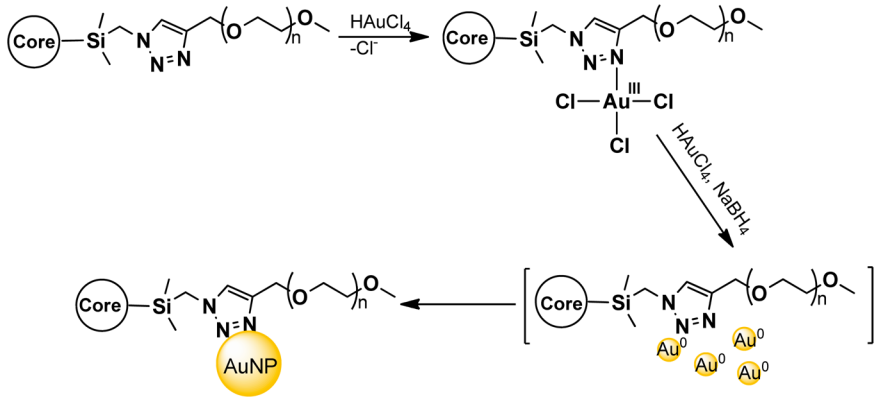
Scheme 3. Synthesis of PEG-Branched Dendrimers DEND550 ($n$ = 11, 12) and DEND2000 ($n$ = 40−44) by "Click" Reactions




Scheme 4. Synthesis of AuNPs: Complexation Process of Au(III) with trz Ring, Reduction of Au(III) by $NaBH_4$, and Gathering of Au(0) into AuNPs




veniently carried out by a selective "click" reaction (Scheme 3) through grafting PEG alkyne onto an azido-terminated nonadendrimer. The classic Sharpless catalyst was used, and the "click" reaction was launched in THF/$H_2O$ solution. These reactions were completed within 48 h, this long reaction time being necessary because of the steric bulk of the PEG tethers and the modest reactivity of Cu(I) under these conditions. By employing PEG alkyne with different chain lengths (PEG550 and PEG2000), two corresponding PEG-branched dendrimers (abbreviated as DEND550 and DEND2000) were obtained in satisfactory yields and characterized by $^1$H, $^{13}$C, and $^{29}$Si NMR, IR spectroscopy, elemental analysis, size exclusion chromatograph, and mass spectrometry for DEND550 (see details in the Supporting Information).

**Preparation and Characterization of the Dendrimer-Stabilized AuNPs.** AuNPs stabilized by DEND550 and DEND2000 were prepared in aqueous solution with sodium borohydride as reductant as shown in Scheme 4. The dendrimer and $HAuCl_4$ were dissolved together in deionized water and stirred for 30 min in order to ensure access of $AuCl_4^-$ to the trz ring that is wrapped by the PEG chains. A freshly prepared $NaBH_4$ aqueous solution was then added dropwise into the as-prepared solution. The color of the solution gradually turned deep red or purple as AuNPs formed. For the purpose of synthesizing AuNPs with various sizes, the molar ratio of Au(III)/trz was varied as 1:1, 5:1, 10:1, and 20:1. Accordingly, the obtained AuNPs with DEND550 are named Au-DEND550-1, Au-DEND550-5, Au-DEND550-10, and Au-DEND550-20, respectively, whereas with DEND2000 they are named Au-DEND2000-1, Au-DEND2000-5, Au-DEND2000-10, and Au-DEND2000-20, respectively.

Complexation of Au(III) with triazole molecules has been investigated by Bortoluzzi and co-workers.[24] In order to understand the complexation process between Au(III) and the trz dendrimers, a titration process was carried out by adding various amounts of $HAuCl_4$ into an as-prepared $D_2O$ solution of dendrimer. After stirring for 20 min, the reaction was monitored by $^1$H NMR spectroscopy. The ratio of trz/Au(III) was progressively set to 1:0, 1:1, and 1:2. $^1$H NMR spectroscopy demonstrated that with both DEND2000 and DEND550 the complexation of Au(III) was complete after addition of 1 equiv of Au(III) per dendritic branch. As depicted in the $^1$H NMR spectrum of DEND2000 in Figure 1, the chemical shift of the trz proton ($H_{trz}$) is 7.9 ppm in pure $D_2O$ solution. After addition of 1 equiv of Au(III) per dendritic branch, the $H_{trz}$ signal is entirely shifted to 8.37 ppm, indicating completion of the complexation. No further shift was observed after addition of another equivalent of Au(III) precursor. The same result was obtained upon complexation of Au(III) with DEND550 (Supporting Information, Figure S11). For comparison, a monomeric trz derivative containing PEG2000 and an alkyl chain was synthesized, and with this monomer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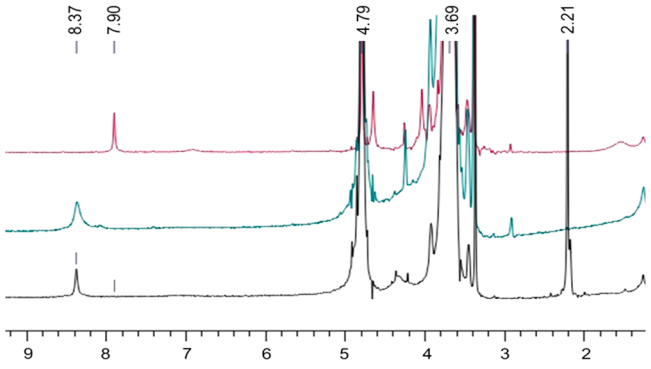


**Figure 1.** $^1$H NMR spectrum of DEND2000 (in red) and $^1$H NMR spectra of DEND2000 after titration of $HAuCl_4$ (to form a trz/Au(III) ratio of 1:1 (in blue) and 1:2 (in black), individually). All the samples were prepared in $D_2O$, and a few drops of acetone-$d_6$ were added in the case of 1:2 DEND2000/Au(III) in order to solubilize all the components.

incomplete complexation resulting from an equilibrium was observed with the use of 1 equiv of Au(III) (Supporting Information, Figure S12). This comparison shows the benefit of the dendrimer structure over a linear analogue, owing to the additional driving force provided by encapsulation of the $Cl_3$Au-trz moieties.

UV−vis spectroscopy also revealed that during the trz complexation the absorbance intensity of Au(III) at 302 nm decreased with time in both Au(III)/DEND2000 and Au(III)/DEND550 solutions. No further decrease of the absorbance was observed after 20 min, suggesting that the complexation reached the equivalence point (Supporting Information, Figure S13). Therefore, it was necessary to leave enough time for the complexation, because the steric effect of both the dendritic structure and the package of PEG chain surrounding the trz ring slowed the coordination process.

In the case of the preparation of AuNPs involving lower Au(III)/trz ratios, the Au atoms were coordinated by trz, leading to the formation of AuNPs of small size with narrow dispersity. It seems reasonable to infer that, given their small size and formation from $Cl_3$Au-trz moieties localized inside the dendrimers, these small AuNPs were encapsulated inside the dendrimers that were much larger than these AuNP cores (Figure 2, left). On the contrary, the AuNPs that were prepared with a high Au(III)/trz ratio mostly resulted from the formation of Au atoms outside the dendrimers because of the excess of Au(III) precursors over the number of trz rings. In this case the interdendritic AuNP stabilization does not prevent the formation of large AuNPs, and such AuNPs are much too large to be encapsulated inside the dendrimers. Thus, the stabilization of these latter AuNPs is due to several surrounding dendrimers (Figure 2, right).

The morphology and the core size of AuNPs were revealed by TEM images, in which the core diameter of the AuNPs was shown to regularly increase as the Au(III)/trz ratio was raised (Table 1 and Supporting Information, Figure S17−20). It was also found that with a certain Au(III)/trz ratio AuNPs stabilized by several dendrimers were diverse in core size, which was attributable to the difference in package density of dendrimers that influenced the mobility of Au(III), $NaBH_4$, and AuNPs, as well as the leaching of Au atoms and small Au clusters. Upon stoichiometric addition of Au(III) to the dendrimeric trz bearing long PEG-2000 tethers followed by reduction with $NaBH_4$, the formed AuNPs have a diameter of 1.8 nm, with about 180 Au atoms, which corresponds to one AuNP formed from Au atoms coming from 20 dendritic macromolecules on average. On the other hand, with short PEG-550 tethers AuNPs are interdendritically formed and stabilized with a 3.2 nm AuNP core, i.e., contain about 1000 Au atoms provided by more than 100 dendrimers (Figure 3 and Table 1). From these experiments, it is concluded that the Au atoms and very small primary Au clusters show a great mobility

**Table 1. TEM and SPB Data for the Dendrimer-Stabilized AuNPs**

| AuNPs | SPB (nm) | TEM ($d$ = nm) | Au atoms/NP[25] |
|---|---|---|---|
| Au-DEND550-1 | 516 | 3.2 | 1000 |
| Au-DEND550-5 | 535 | 7.3 | 12 000 |
| Au-DEND550-10 | 537 | 9 | 22 000 |
| Au-DEND550-20 | 538 | 12 | 53 000 |
| Au-DEND2000-1 | | 1.8 | 180 |
| Au-DEND2000-5 | 526 | 5.7 | 5700 |
| Au-DEND2000-10 | 529 | 8.7 | 20 200 |
| Au-DEND2000-20 | 538 | 11.4 | 45 000 |

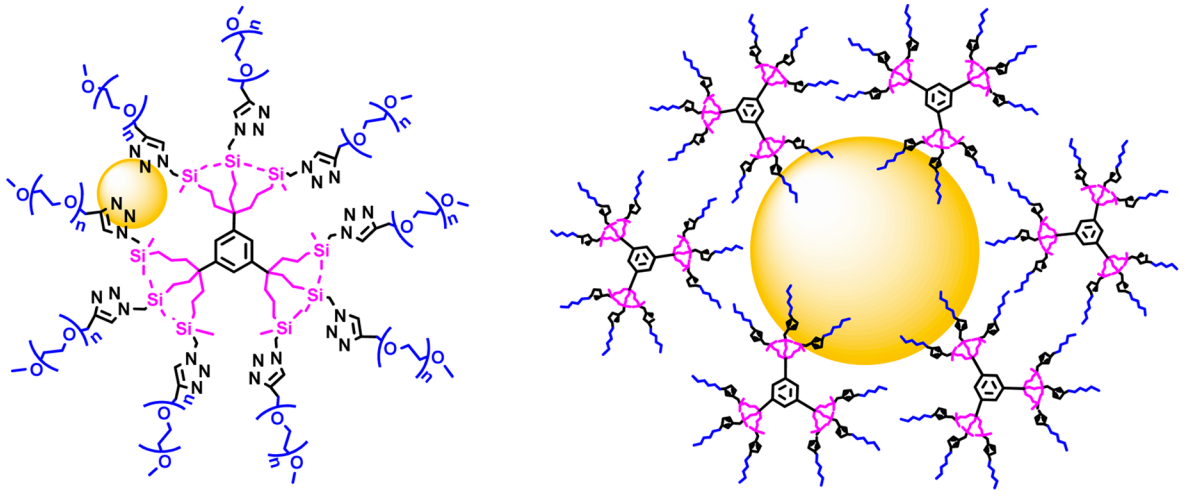

**Figure 2.** Dendrimer-encapsulated small AuNP (left) and large AuNP surrounded by several dendrimers (right).


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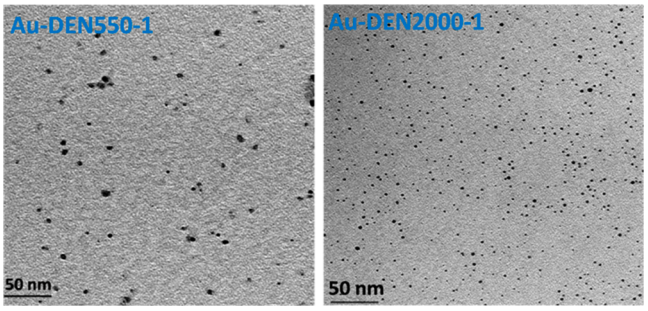


**Figure 3.** TEM images of Au-DEND550-1 ($d$ = 3.2 nm) and Au-DEND2000-1 ($d$ = 1.8 nm).

before definitive stabilization. The filtering effect of the PEG tethers is also clearly demonstrated upon comparing the influence of two PEG tether lengths on the limitation of the AuNP size.

The UV−vis spectra of the AuNPs displayed changes in the surface plasmon band (SPB) along with the variety of sizes. For instance, the SPB of Au-DEND550-1 was observed at a maximum of 516 nm, while the SPB of Au-DEND550-20 was found at 538 nm (Supporting Information, Figure S14). The difference in SPB was in agreement with the variation of core diameter as revealed by TEM. The plasmon band of Au-DEND2000-1 was weak and unresolved in the UV−vis spectrum, indicating that Au-DEND2000-1 has a small core size (1.8 nm). These AuNPs were also narrowly dispersed in aqueous solution, as revealed by the DLS measurements (Supporting Information, Figures S15 and S16). This result suggests promising applications of click-PEG-dendrimer-stabilized AuNPs in aqueous media.

**Catalytic Reduction of *p*-Nitrophenol.** Nitrophenols are toxic and hazardous micropollutants, and their degradation is challenging for environmental purposes. On the other hand, *p*-aminophenol is a potential industrial intermediate in manufacturing various analgesic and antipyretic drugs, anticorrosion lubricants, and hair-drying agents; thus efficient PdNP catalysis of *p*-nitrophenol reduction is of great value. *p*-Nitrophenol reduction also is a versatile reaction that is useful for the evaluation of the catalytic activity of various metal NPs, owing to its high sensitivity to metal catalyst and the convenient determination of the reaction rate through UV−vis spectroscopy.[26] It has been previously reported that AuNPs possessed prominent catalytic activity in *p*-nitrophenol reduction.[27] In this context the loose coordination of trz ligands to the AuNP core surface provides a very favorable situation for efficient catalysis. The influence of the morphology of dendrimers, the size of AuNPs, and the catalyst amount on the kinetics of *p*-nitrophenol reduction was investigated in this study. Thus, the relatively smaller AuNPs, Au-DEND550-1 ($d$ = 3.2 nm) and Au-DEND550-5 (7.3 nm), as well as Au-DEND2000-1 (1.8 nm) and Au-DEND2000-5 (5.7 nm), were provided as catalysts for the *p*-nitrophenol reduction. A typical catalytic reaction was processed as follows: a *p*-nitrophenol (0.09 $\mu$mol) aqueous solution was mixed with sodium borohydride (7.2 $\mu$mol) in a 3 mL standard quartz cuvette, to form a total volume of 2.5 mL. This solution immediately turned yellow and showed an intense absorption at 400 nm in the UV−vis spectrum. Various molar percentages of AuNPs (0.5%, 1%, 2%, and 5%, separately) in aqueous solution were then injected into the above-mentioned quartz cuvette, and the reduction reaction was monitored by UV−vis spectroscopy every 40 s throughout the reduction process (see Supporting Information, Figures S21−24).

The plot of the consuming rate $[-\ln(C/C_0)]$ of *p*-nitrophenol versus the reaction times is presented in Figure 4, and the $k$ values of the reduction under various conditions

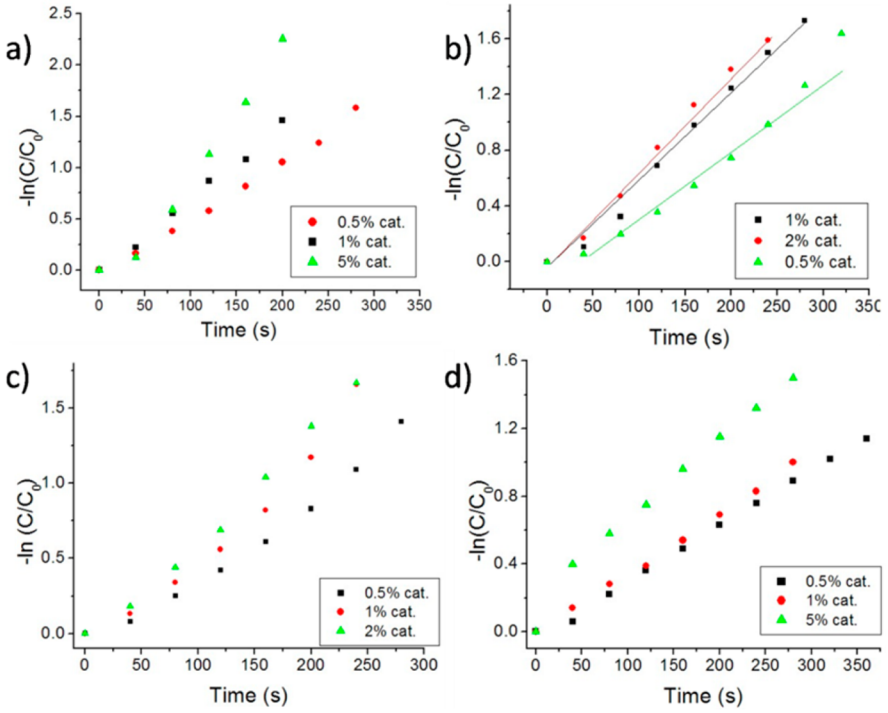


**Figure 4.** Plots of the consuming rate of *p*-nitrophenol $[-\ln(C/C_0)]$ vs the reaction times with various AuNPs as catalysts: (a) Au-DEND550-1, (b) Au-DEND550-5, (c) Au-DEND2000-1, (d) Au-DEND2000-5.


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are summarized in Figure 5. The catalysis results obtained with Au-DEND550-1 (3.2 nm) and Au-DEND550-5 (7.3 nm) show

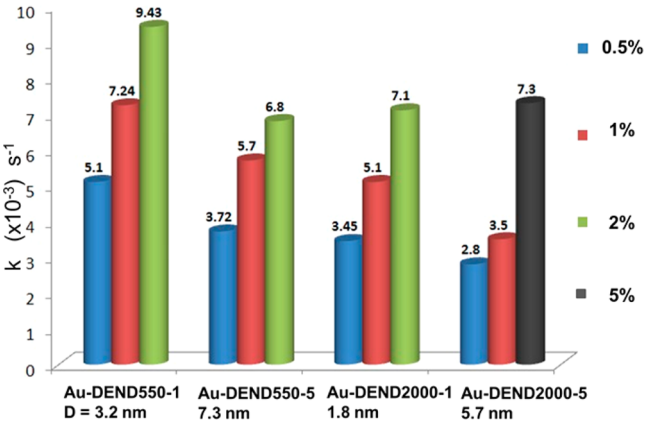


**Figure 5.** Bar graph showing the kinetic constant ($k$ value) of *p*-nitrophenol reduction with various AuNP catalysts.

that the $k$ value increases upon raising the amount of catalyst, and the $k$ value decreases upon raising the AuNP size (Figure 5). Likewise, the large dendrimer (DEND2000)-stabilized AuNPs, Au-DEND2000-1 (1.8 nm) and Au-DEND2000-5 (5.7 nm), exhibit a similar trend.

Upon comparing the catalysis results of four AuNPs (Figure 5), it obviously appears that AuNPs stabilized by the small dendrimer (DEND550) exhibit higher catalytic activity than AuNPs stabilized by the larger dendrimer (DEND2000). This is taken into account by the less bulky periphery of the small dendrimer (DEND550) that allows easier access of the substrates to the AuNP core surface and makes their reaction easier on this surface. On the other hand, the filtering effect of the large PEG tethers in the case of PEG2000 causes kinetic limitations. In other reported examples of AuNP-catalyzed *p*-nitrophenol reduction, the structural transformation at the AuNP surface was found to be rate limiting,[27] whereas here the diffusion of the substrate through the ligand shell can control the kinetics when the PEG tethers are long enough. In particular, Au-DEND550-1 (3.2 nm) displays a remarkable catalytic efficiency ($k = 5.1 \times 10^{-3}$ $s^{-1}$, with the catalyst amount 0.5%) in such a low concentration of *p*-nitrophenol. This efficiency is among the best ever observed for this reaction, which can be attributed to the very mild interaction between the trz nitrogen ligand and the AuNP core surface, causing a very easy ligand exchange between the trz ligand and the substrate (*p*-nitrophenol and $NaBH_4$).

**Concluding Remarks.** The facile "click" synthesis of nona-PEG-branched macromolecules offers a valuable straightforward application of the $\eta^5$-$C_5H_5Fe^+$-induced nona-allylation of mesitylene. Then a positive and productive dendritic effect was disclosed for the quantitative intradendritic trz complexation to Au(III) upon reaction of the click dendrimers with $HAuCl_4$ in water according to $AuCl_4^- + trz \rightarrow AuCl_3(trz) + Cl^-$, whereas under analogous conditions complexation of a nondendritic triazole analogue leads only to an equilibrium.

Another original dendritic effect is that involving the influence of the PEG tether length on the formation of the AuNPs, in particular on their size. The $NaBH_4$ reduction of triazole-coordinated Au(III) was shown to lead to relatively small AuNPs, contrary to the reduction of free $HAuCl_4$ (when the Au(III)/triazole ratio was larger than unity), which led to large AuNPs. The influence of the parameters involved in the AuNP formation leads to the conclusion that interdendritic mobility of Au atoms (or native Au clusters) occurs more readily than in the case of PdNPs, which is of interest for late transition metal nanoparticle engineering for catalysis. Finally these trz dendrimer-stabilized AuNPs are excellent *p*-nitrophenol reduction catalysts.

In summary, the stabilization of metal NPs by easily synthesized "click" arene-cored trz dendritic macromolecules produces nanoreactors for nanoparticle catalysis with great efficiency thanks to the combination of the dendrimer-supported nanoreactor and the flexible Au–trz bonding. The control of the fate of native Au atoms and small Au clusters by the structural and reaction parameters including "forced" leaching from the dendrimers has led to an understanding of how to optimize the catalytic efficiencies.

## EXPERIMENTAL SECTION

**Chemicals and Characterization Tools.** All solvents and chemicals were used as purchased. Milli-Q water (18.2 MΩ) was used in the preparation of AuNPs. NMR spectra were recorded at 25 °C with a Bruker 300 (300 MHz) spectrometer. All the chemical shifts are reported in parts per million ($\delta$, ppm) with reference to $Me_4Si$ for the $^1H$ and $^{13}C$ NMR spectra. The infrared (IR) spectra were recorded on an ATI Mattson Genesis series FT-IR spectrophotometer. UV–vis absorption spectra were measured with a PerkinElmer Lambda 19 UV–vis spectrometer. Elemental analyses were recorded on a PAR 273 potentiostat under a nitrogen atmosphere. The DLS measurements were made using a Malvern Zetasizer 3000 HSA instrument at 25 °C at an angle of 90°. Size exclusion chromatography of dendrimers was performed using a JASCO HPLC pump type 880-PU, TOSOHAAS TSK gel columns (G4000, G3000, and G2000 with pore sizes of 20, 75, and 200 Å, respectively, connected in series), and a Varian (series RI-3) refractive index detector, with THF as the mobile phase and calibrated with polystyrene standards

**Synthesis of DEND550 and DEND2000.** A general procedure was employed and is described below: the azido-terminated nonabranch dendrimer **3**[11] (0.08 mmol, 121 mg) and propargyl PEG (0.72 mmol) were dissolved in 5 mL of THF. $CuSO_4 \cdot 5H_2O$ (0.72 mmol, 180 mg) in aqueous solution was then added. The obtained solution was deaerated and refilled with $N_2$, followed by dropwise addition of a freshly prepared aqueous solution of sodium ascorbate (1.44 mmol, 285 mg) to obtain a 1:1 THF/water ratio. The solution was stirred for 48 h at room temperature under a $N_2$ atmosphere. After removal of THF in vacuum, 5 mL of $CH_2Cl_2$ and 5 mL of concentrated (30%) aqueous ammonia solution were added. The mixture was stirred for 30 min to release the Cu ions trapped inside the polymer as $[Cu(NH_3)_2(H_2O)_2]^{2+}$. Then the organic layer was collected and washed with brine. After drying with anhydrous $Na_2SO_4$, the solvent was removed under vacuum. DEND2000 was recovered and purified by reprecipitation in $CH_2Cl_2$ and diethyl ether. The PEGylated dendrimers were obtained in 91% (DEND550) and 88% (DEND2000) yields, respectively.

**Titration of $HAuCl_4$ into the $D_2O$ Solution of Dendrimers (or Monomer).** Taking Au(III)/DEND2000 as an example, $HAuCl_4$ (0.01 mmol, 2 mg, 1 equiv per branch) was added into a $D_2O$ solution of DEND2000 (0.0011 mmol, 21 mg, in 1 mL of $D_2O$). After stirring for 20 min, the $^1H$ NMR spectrum (300 MHz) was recorded. Then, another equivalent of $HAuCl_4$ was added into the above-mentioned solution, this solution was further stirred for 20 min, and the $^1H$ NMR spectrum was recorded again. The same operation was followed in the titration of $HAuCl_4$ with DEND550 (or the trz monomer) in $D_2O$ solution.

**Preparation of Dendrimer-Stabilized AuNPs.** AuNPs stabilized by dendrimers DEND550 (respectively DEND2000) were prepared under various Au(III)/trz ratios (1:1, 5:1, 10:1, and 20:1, respectively). Typically, $HAuCl_4 \cdot 3H_2O$ (0.009 mmol, 3.5 mg) and DEND550 (0.001 mmol, 6.5 mg) were dissolved in 5 mL of Milli-Q water. After being


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stirred for 10 min, 1 mL of freshly prepared $NaBH_4$ (0.045 mmol, 1.7 mg) water solution was added dropwise into the solution with vigorous stirring. The Au-DEND550-1 solution that was obtained was further stirred for 30 min and was dialyzed against a large volume of water (2 × 4 h). Subsequently, Au-DEND550-5, Au-DEND550-10, Au-DEND550-20, Au-DEND2000-1, Au-DEND2000-5, Au-DEND2000-10, and Au-DEND2000-20 were prepared following the same procedure. These dendrimer-stabilized AuNPs were kept in aqueous solution and were diluted before characterization and use in catalytic reactions.

**Catalytic Reduction of *p*-Nitrophenol with Dendrimer-Stabilized AuNPs.** An aqueous solution (2.5 mL) containing 0.09 μmol of *p*-nitrophenol and 7.2 μmol of $NaBH_4$ was prepared in a 3 mL standard quartz cuvette (path length: 1 cm). Then AuNP (0.5%, 0.45 × $10^{-3}$ μmol) catalyst was injected into the as-prepared solution, and the reaction progress was detected by UV−vis spectroscopy every 40 s. The same processes were carried out with an increasing catalyst amount, successively 1%, 2%, and 5%.

## ■ ASSOCIATED CONTENT

### Supporting Information

Characterization data of dendrimers and AuNPs and UV−vis spectroscopic studies of the catalytic *p*-nitrophenol reduction reactions. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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