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Synthesis, Characterization, and Surface Immobilization of Metal Nanoparticles Encapsulated within Bifunctionalized Dendrimers

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Bifunctionalized poly(amidoamine) dendrimers having both quaternary ammonium groups and primary amines on their periphery were prepared. Pd and Pt nanoparticles were encapsulated within these dendrimers by extraction of the metal ions into their interior, followed by chemical reduction. The high positive charge on the surface of these dendrimers reduces the likelihood of agglomeration, and the unquaternized amine groups provide a reactive handle for immobilizing the dendrimer-encapsulated nanoparticles (DENs) onto surfaces. High-resolution transmission electron microscopy images reveal that both encapsulated Pd and Pt nanoparticles are nearly monodisperse with an average diameter of 1.7 ± 0.3 nm. Pd and Pt DENs were immobilized onto Au surfaces using an intermediary self-assembled monolayer as an adhesion layer. Only a small fraction of the resulting nanoparticle monolayer is lost when sonicated in an acidic aqueous solution or subjected to electrochemical cycling.

Introduction

Here, we report on the advantages of using partially quaternized poly(amidoamine) (PAMAM) dendrimers for preparing dendrimer-encapsulated nanoparticles (DENs) and for linking DENs to surfaces. Specifically, we have found that DENs prepared using amine-terminated PAMAM dendrimers that have been partially quaternized (Gn-Q$_p$, where n is the dendrimer generation and p is the number of the peripheral amine groups that have been quaternized) lead to formation of Pd and Pt DENs having a significantly narrower size distribution than when these materials are prepared using commercially available PAMAM dendrimers. Moreover, because the surface of Gn-Q$_p$ bifunctional dendrimers is only partially quaternized, the remaining amine groups can be used to covalently link DENs to other polymers, biomolecules, or, as we show here, monolithic solid surfaces.

Nanometer-scale metal and semiconductor particles sometimes exhibit unique physical or chemical properties that are interesting in their own right but that also hold out the promise of technological advances in fields such as catalysis, sensors, electronics, and biotechnology.[1−3] Applications such as these require simple synthetic approaches for preparing highly uniform nanomaterials. A number of methods have been reported for preparing metal nanoparticles in the <3 nm size range,[4,5] but only a few of these result in materials having monodispersities in the range of ±20%.[6−8] In addition to uniformity, many technological applications also require that nanomaterials be linked to one another or to monolithic solid supports.[9−11] Typical methods for immobilizing nanoparticles onto surfaces involve adsorption onto substrates coated with functional groups that induce electrostatic interactions[12−14] or covalent bonds[15−23] between the nanoparticle and the surface.

Dendrimers have been used as templates for preparing metallic, bimetallic, and semiconductor nanoparticles.[24−26] DENs are prepared in a two-step process. First, metal ions are sequestered within the dendrimer, and then the ions are chemically reduced. Because the synthesis relies on dendrimeric templates, the resulting metal nanopar-

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ticles (the replicas) can be quite monodisperse in size. The ability of high-generation PAMAM dendrimers to host Cu, Pd, Pt, Ag, and Au nanoparticles is attributable to the spheroidal structure of the dendrimer, which contains void spaces and functional groups that are able to complex with metal ions.[6,27−32] The properties of metal−dendrimer nanocomposites depend on the nature of the terminal groups of the dendrimers. For example, amine peripheral groups usually (but not always)[33] induce agglomeration and precipitation of large metal clusters. This is most likely because many metal ions complex with the periphery of amine-terminated dendrimers, which typically results in rather large (>5 nm) metal clusters stabilized by multiple dendrimers.[34]

One approach for preventing metal-ion complexation is to selectively protonate peripheral primary amine groups.[35,36] However, this requires a restrictive pH window, which can be a nuisance for many applications. Accordingly, dendrimers having noncomplexing functional groups on their periphery, such as hydroxyl-terminated PAMAM dendrimers, are most often used for preparing relatively small (<2 nm), and in some cases nearly size-monodisperse, DENs. However, there are two drawbacks to using hydroxyl-terminated dendrimer for preparing DENs. First, hydroxyl groups themselves are fairly good reducing agents.[30,37] This makes it very difficult to prepare, for example, monodisperse Au DENs using hydroxyl-terminated dendrimers.[38] Second, hydroxyl groups are not very reactive, which makes it difficult to covalently link DENs prepared within such materials to other molecules or objects in aqueous solvent. Note, however, that such materials have been immobilized on solid surfaces by electrostatic interactions.[39−44]

This paper describes the use of dendrimers for templating, stabilizing, and immobilizing onto surfaces 1−2 nm diameter metal nanoparticles having a narrow size distribution. Specifically, we found that partially quaternized PAMAM dendrimers are an attractive template for preparing highly monodisperse Pd and Pt nanoparticles, because the high positive charge at the dendrimer periphery prevents metal-ion-induced interdendrimer agglomeration. In addition, Pd and Pt DENs prepared within Gn-Q$_p$ dendrimers can be immobilized onto Au surfaces via covalent amide bond formation between the unquaternized amine groups on the dendrimer periphery and anhydride-activated self-assembled monolayers (SAMs). In this approach, the dendrimers act as a mediator for linking metal nanoparticles to monolithic solid surfaces. Pd and Pt DEN monolayers prepared in this way were found to be quite stable.

Experimental Section

Chemicals and Materials. Fourth-generation poly(amidoamine) (PAMAM) dendrimers having amine terminal groups (G4-NH$_2$) were obtained from Dendritech, Inc. (Midland, MI), as a 17.3% wt/wt solution in methanol. The methanol was removed under vacuum prior to use. The following chemicals were used as received: glycidyltrimethylammonium chloride (∼90%, Fluka Chemie AG), K$_2$PdCl$_4$ (99.99%, Aldrich Chemical Co., Milwaukee, WI), K$_2$PtCl$_4$ (99.9%-Pt, Strem Chemicals, Inc., Newburyport, MA), NaBH$_4$ (99%, Aldrich), methanol (EM Science), mercaptoundecanoic acid (MUA) (95%, Aldrich), ethyl chloroformate (97%, Aldrich), 4-methylmorpholine (99%, Aldrich), and CHCl$_3$ (99.8%, EM Science). Cellulose dialysis sacks having a molecular weight cut off of 1.2×10^4 were purchased from Sigma Diagnostics, Inc. (St. Louis, MO). Water (18 MΩ·cm, Milli-Q, Millipore, Bedford, MA) was used to prepare aqueous solutions. Au-coated substrates were prepared by electron-beam evaporation of 10 nm of Ti followed by 200 nm of Au onto Si(100) wafers (Lance Goddard Associates, Foster City, CA). The wafers were subsequently diced into 2.6 cm × 1.3 cm pieces. Before each experiment all wafers were cleaned in a low-energy ozone cleaner for 10 min (Boekel Industries, Inc., model 135500).

Synthesis of Polycationic Dendrimers. Partially quaternized, fourth-generation PAMAM dendrimers (G4-Q$_p$) were prepared by reacting G4-NH$_2$, which carries 64 terminal primary amines, with 64 equiv of glycidyltrimethylammonium chloride. The synthetic procedure used is similar to one previously reported in the literature.[45] G4-NH$_2$ (0.39 g, 27.4 μmol) was dissolved in 10 mL of methanol, and 0.27 g (1.75 mmol) of glycidyltrimethylammonium chloride was added dropwise with stirring. The reaction mixture was stirred for 2 days at 40 °C, and then methanol was removed by rotary evaporation. The crude product was redissolved in 30 mL of water, and the solution was purified by dialysis against water for 24 h. The final product was dried in a vacuum to give 0.5 g (96% yield) of G4-Q$_{32}$ as a white viscous solid. With the same synthetic procedure, G6-Q$_{116}$ was prepared by reaction of G6-NH$_2$ with 256 equiv of glycidyltrimethylammonium chloride (97% yield). The chemical structures of G4-Q$_{32}$ and G6-Q$_{116}$ were confirmed by ^{1}H and ^{13}C NMR and (for G4-Q$_{32}$) MALDI-MS spectra (see the Supporting Information).

Characterization and Instrumentation. ^{1}H and ^{13}C NMR spectra were collected on a Varian Inova 500 MHz spectrometer at 500.1 and 125.8 MHz, respectively. CD$_3$OD was used as an internal standard for the NMR analyses. MALDI-MS spectra were recorded on a Voyager Elite XL MALDI time-of-flight mass spectrometer outfitted with a 337 nm pulsed nitrogen laser. 2′,4′,6′-Trihydroxyacetophenone was used as the MALDI matrix. Complexation between aqueous metal ions and dendrimers was monitored with an HP8453 UV−vis absorption spectrophotometer. High-resolution transmission electron micrographs (HRTEMs) were obtained using a JEOL-2010 transmission electron microscope having a point-to-point resolution of 0.19 nm. Samples were prepared by placing a drop of DEN solution on a carbon-coated Cu TEM grid (400 mesh, Electron Microscopy Science, Fort Washington, PA) and allowing the solvent to evaporate in air. FTIR-external reflection spectroscopy (FTIR-ERS) measurements were carried out using an FTS-6000 spectrometer (Bio-Rad, Cambridge, MA) equipped with a Harrick Scientific Seagull reflection accessory (Ossining, NY) and a liquid-N$_2$-cooled, narrow-band MCT detector. All spectra were obtained at 4 cm^{-1} resolution using p-polarized light at an 84° angle of incidence with respect to the substrate normal. Electrochemical experiments were performed in a single-compartment, glass cell using a standard three-electrode configuration with a Pt-gauze counter electrode and a Ag/AgCl (3 M NaCl) reference electrode (Bio-

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analytical Systems, West Lafayette, IN). Cyclic voltammetry was performed using a computer-controlled potentiostat (model 660A, CH Instruments, Austin, TX) to monitor the stability of DENs on Au surfaces.

Preparation of Dendrimer-Encapsulated Pd and Pt Nanoparticles. The preparation of G4-Q$_{32}$/Pd and G4-Q$_{32}$/Pt DENs followed procedures we have previously reported for preparing metal nanoparticles encapsulated within hydroxyl-terminated PAMAM dendrimers (G4-OH).[6,28,46] Briefly, to 8.9 mL of water was added 0.5 mL of a 1 mM G4-Q$_{32}$ aqueous solution and, subsequently, 0.2 mL of a 0.1 M K_2PdCl_4 (or 0.1 M K_2PtCl_4) aqueous solution. After the mixture was stirred for 30 min (or 48 h in case of K_2PtCl_4), 0.4 mL of a 1.0 M $NaBH_4$ aqueous solution was added. The resulting dark brown solution was purified by dialysis against water for 18 h to give G4-Q$_{32}$(Pd$_{40}$) (or G4-Q$_{32}$-(Pt$_{40}$)), which contain an average of 40 metal atoms per dendrimer.

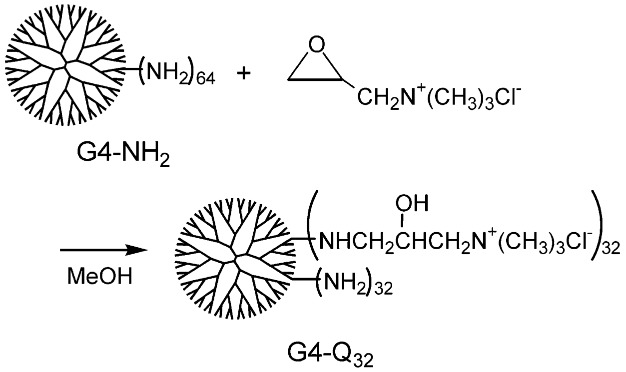
Surface Modification. Surface-immobilized DENs were prepared by covalently linking G4-Q$_{32}$(Pd$_{40}$) to a self-assembled mercaptoundecanoic acid (MUA) monolayer. The monolayer was prepared by immersing an ozone-cleaned Au substrate in a 1 mM ethanol solution of MUA for 6 h. The resulting MUA SAM was activated in a $CHCl_3$ solution containing 10 mM ethyl chloroformate and triethylamine for 1 h.[47,48] DENs were covalently linked to the activated monolayer by soaking it in a 5 mM aqueous solution of G4-Q$_{32}$(Pd$_{40}$) for 6 h, followed by rinsing with water and ethanol, and then drying with N_2. As a control experiment to confirm covalent attachment of DENs, G4-Q$_{32}$-(Pd$_{40}$) monolayers on MUA SAMs were prepared using the same procedure, but activation with ethyl chloroformate was omitted.

Results and Discussion

Synthesis of Polycationic, Bifunctionalized Dendrimers. Our objective in this work was to develop a dendrimer that could serve as a template for preparing DENs and also have a sufficiently reactive periphery that it could subsequently be covalently attached to solid surfaces, biomolecules, or other types of polymers. We reasoned that partial quaternization of amine-terminated PAMAM dendrimers would be the simplest way to achieve this goal for the following reasons. First, modification of the periphery should not change the desirable templating properties of the PAMAM interior. Second, partial quaternization of the periphery should prevent interdendrimer complexation of metal ions because of the poor metal-ion complexing ability of quaternized amines,[49,50] and because of electrostatic repulsion between positively charged dendrimers. Note that in the absence of quaternization, except over a fairly narrow pH range,[36] the surface of amine-terminated dendrimers has a strong affinity for many types of metal ions. This leads to interdendrimer cross-linking and subsequent precipitation, and therefore it is not possible to prepare small, monodisperse DENs.[39] Third, the remaining unquaternized amines on the dendrimer surface should be sufficiently reactive to form covalent bonds under appropriate conditions.

To synthesize polycationic dendrimers, commercially available, fourth-generation, amine-terminated PAMAM dendrimers (G4-NH$_2$) having 64 peripheral amine groups were reacted with glycidyltrimethyammonium chloride to yield pendant quaternary ammonium groups (Scheme 1). The product was characterized by ^1H and ^{13}C NMR and MALDI-MS analyses (see Supporting Information), and the extent of quaternization of the G4-NH$_2$ periphery was calculated from ^1H NMR integration. Comparison of the area of the methine proton ($\delta = 4.28$ ppm) adjacent to the hydroxyl group (Scheme 1) versus the area of the methylene protons ($\delta = 2.42$ ppm) associated with the dendrimer backbone reveals that, on average, ~34 of the amine-terminal groups of G4-NH$_2$ are modified with quaternary ammonium groups (~53% functionalization). MALDI-MS of the functionalized dendrimer reveals the molecular ion peak at 18735 *m*/*z* (see Supporting Information). This value corresponds to G4-NH$_2$ having ~30 quaternary ammonium groups (47% functionalization) on the periphery. We estimate the extent of surface functionalization at 50% by taking the average of the MALDI-MS and NMR data (here we denote this dendrimer as G4-Q$_{32}$). We also prepared the sixth-generation equivalent of G4-Q$_{32}$, G6-Q$_p$, and from NMR, the extent of surface functionalization was estimated to be 45%. It is important to note that although 64 and 256 equiv of the epoxide derivative were used for the synthesis of G4-Q$_p$ and G6-Q$_p$, respectively, the extent of functionalization was still only ~50%. Control experiments indicate that this is a consequence of reduced reactivity of the partially functionalized dendrimer, which in turn is likely due to electrostatic repulsion between positively charged reactants in solution and the partially reacted, positively charged dendrimer surface. For example, the reaction of G4-NH$_2$ with 64 equiv of *tert*-butyl glycidyl ether, which is an uncharged analogue of glycidyltrimethylammonium chloride, results in 100% surface functionalization.

Scheme 1



Preparation and Characterization of Polycationic, Bifunctionalized DENs. The approach for preparing nanoparticles within polycationic dendrimers is similar to that used for hydroxyl-terminated PAMAM dendrimers.[6,28,46] Specifically, metal ions are extracted from solution into the dendrimer interior, and then the encapsulated metal ions are chemically reduced to yield an encapsulated, zerovalent nanoparticle. Figure 1 shows UV−vis absorbance spectra of aqueous dendrimer solutions containing, on average, 40 Pd^{2+} or Pt^{2+} ions (for convenience, we denote all possible complex ions in solution and within the dendrimer as Pd^{2+} or Pt^{2+})[51] encapsulated within each G4-Q$_{32}$ dendrimer before (G4-Q$_{32}$(Pd^{2+})$_{40}$ and G4-Q$_{32}$(Pt^{2+})$_{40}$, respectively) and after (G4-Q$_{32}$(Pd$_{40}$) and G4-Q$_{32}$(Pt$_{40}$), respectively) reduction with BH_4^-. In the case of Pd^{2+} (Figure 1a), an absorption band, which corresponds to the ligand-to-metal charge-transfer transition between Pd^{2+} and tertiary amine ligands within the dendrimer, is present at 225 nm prior to reduction. After chemical reduction, this band is greatly diminished and a featureless interband transition, corresponding to

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[51] $PdCl_4^{2-}$ and $PtCl_4^{2-}$ complex ions can exist in multiple displaced-ligand forms in water and within the dendrimer. Because we do not always know which form is present, we choose to denote all possible complex ions as Pd^{2+} or Pt^{2+} to minimize confusion. For a more in-depth discussion of this point, see ref 52.

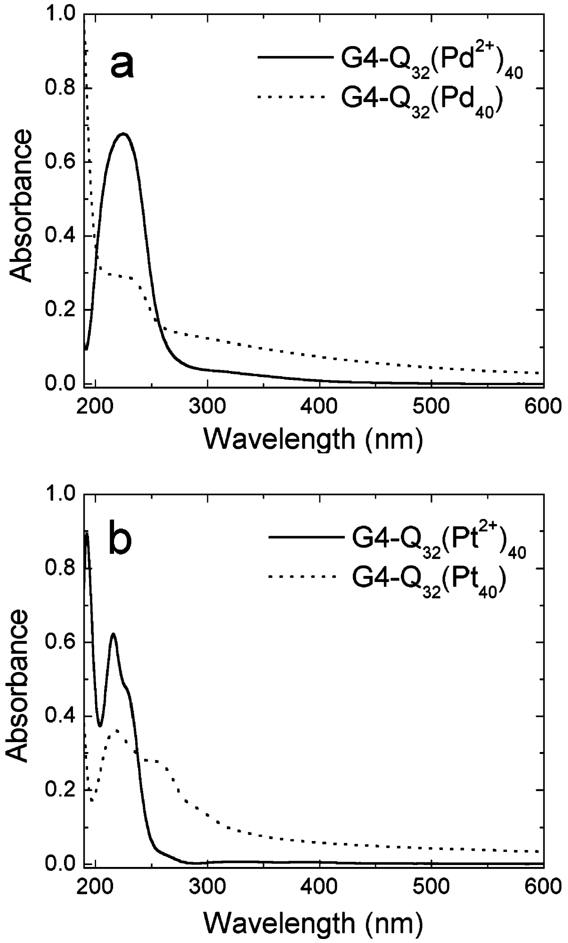

Figure 1. UV−vis absorption spectra of aqueous solutions containing (a) Pd^{2+} and (b) Pt^{2+} and G4-Q_{32} before (solid line) and after (dotted line) chemical reduction with $NaBH_4$. An aqueous solution of G4-Q_{32} was used to obtain the background spectrum.

zerovalent Pd nanoparticles, is observed as a monotonically increasing absorption toward higher energy.[6,52] In addition, the color of the solution turns from pale yellow prior to reduction to dark brown after reduction. No sign of agglomeration or precipitation is observed. Taken together with previous reports of Pd DENs prepared within hydroxyl-terminated PAMAM dendrimers,[6] these results are indicative of encapsulation of Pd nanoparticles within individual dendrimers. Similar spectroscopic behavior (Figure 1b) is observed for G4-Q_{32}(Pt^{2+})$_{40}$ and G4-Q_{32}(Pt_{40}), except that the ligand-exchange reaction that leads to complexation between Pt^{2+} and the dendrimer is much slower.[24,28] Control experiments performed under the same conditions, but using unquaternized G4-NH_2 PAMAM dendrimers, lead to immediate precipitation when the reducing agent is added. These results strongly suggest that repulsive electrostatic interactions between positively charged dendrimers, along with the poor metal-ion complexing ability of quaternized amines, play an important role in preventing agglomeration of metal nanoparticles.[50]

Figure 2 presents HRTEM images and particle size distributions for Pd and Pt nanoparticles prepared within G4-Q_{32}. The images indicate that these particles are well separated, which is a likely consequence of the high electrostatic charge on the host dendrimers, and that they are nearly monodisperse in size. The mean diameters and standard deviations (1σ) for the G4-Q_{32}(Pd_{40}) (Figure 2b) and G4-Q_{32}(Pt_{40}) (Figure 2d) nanoparticles are both 1.7 ± 0.3 nm. Note that all these sizes are significantly larger than expected for a roughly spherical 40-atom metal particle (∼1.1 nm), but the results are fully consistent with our previous results for Pt and Pd DENs prepared within fourth-generation hydroxyl-terminated PAMAM dendrimers (G4-OH).[6,28,46] Specifically, we found that the mean diameters for G4-OH(Pd_{40}) and G4-OH(Pt_{40}) are in the range of 1.3−1.7 nm with standard deviations ranging from ±0.2 to ±0.3 nm.[24] Similarly, Li and El-Sayed prepared G4-OH(Pd_{10}) DENs that were 1.4 ± 0.4 nm in diameter.[7] Note that Au nanoparticles prepared in either G4-Q_{32} or G6-Q_{116} have sizes that correspond nearly exactly with expectations.[53] This suggests that there is something peculiar about Pt and Pd DENs that we do not understand at the present time.

Surface Immobilization of Polycationic, Bifunctionalized DENs. Previous studies have shown that amine-terminated dendrimers can be easily covalently linked to Au surfaces via an intermediary SAM adhesion layer.[47,48] The method involves formation of a mercaptoundecanoic (MUA) SAM on an Au surface, activation of the distal carboxylic acid groups using ethyl chloroformate, and then reaction of this activated monolayer with primary amine groups on the dendrimer periphery. We thought it would be possible to use this same approach (Scheme 2) to link G4-Q_{32}(Pd_{40}) DENs to Au surfaces, because G4-Q_{32} contains ∼32 unfunctionalized primary amine groups at its periphery. The spectra shown in Figure 3 confirm this expectation. Spectrum a was obtained from the activated MUA SAM. The peaks at 1822 and 1746 cm^{-1} correspond to the anhydride carbonyl bands.[54] After reaction of the activated SAM with G4-Q_{32}(Pd_{40}) in water, these bands are replaced by three new peaks at 1723, 1661, and 1560 cm^{-1} (spectrum b). The peak at 1723 cm^{-1} arises from the carbonyl band of MUA, which is present as a consequence of partial hydrolysis of the activated monolayer.[48] The appearance of the amide I and II peaks at 1661 and 1560 cm^{-1}, respectively, arises from both the internal structure of G4-Q_{32} and the amide bonds formed by the reaction between the anhydride-activated SAM and the peripheral amines of G4-Q_{32}. It is possible to estimate the dendrimer surface coverage by comparing the amide-band intensity to that of a full dendrimer monolayer physisorbed to a Au surface.[55] The results indicate that ∼40% of maximum DEN coverage is attained in the experiment represented by Figure 3b.

The presence of metal nanoparticles on the MUA SAM was confirmed by X-ray photoelectron spectroscopy (XPS). The XPS analysis was carried out using G4-Q_{32}(Pt_{40}) instead of G4-Q_{32}(Pd_{40}), because the Pd($3d_{5/2}$) peak overlaps with the Au($4d_{5/2}$) substrate peak. The important point is that the XPS spectrum of G4-Q_{32}(Pt_{40}) immobilized on an anhydride-activated MUA SAM provides clear evidence for the presence of zerovalent Pt in the monolayer (see Supporting Information).

To confirm robust attachment of G4-Q_{32}(Pd_{40}) to the SAM, we carried out a series of experiments to test the stability of the DEN monolayers. First, because we are interested in using surfaces such as these for electrocatalysis, we investigated the effect of electrochemical potential on the stability of the monolayer. As shown in spectrum c in Figure 3, the magnitude of the amide I peak

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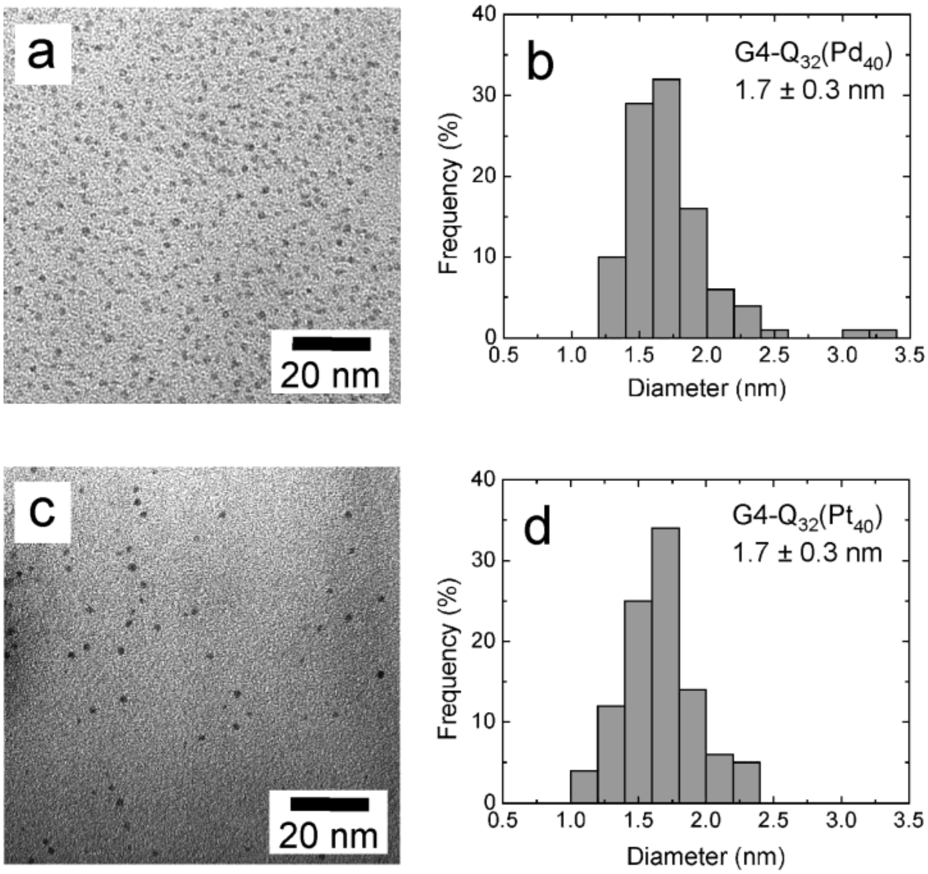
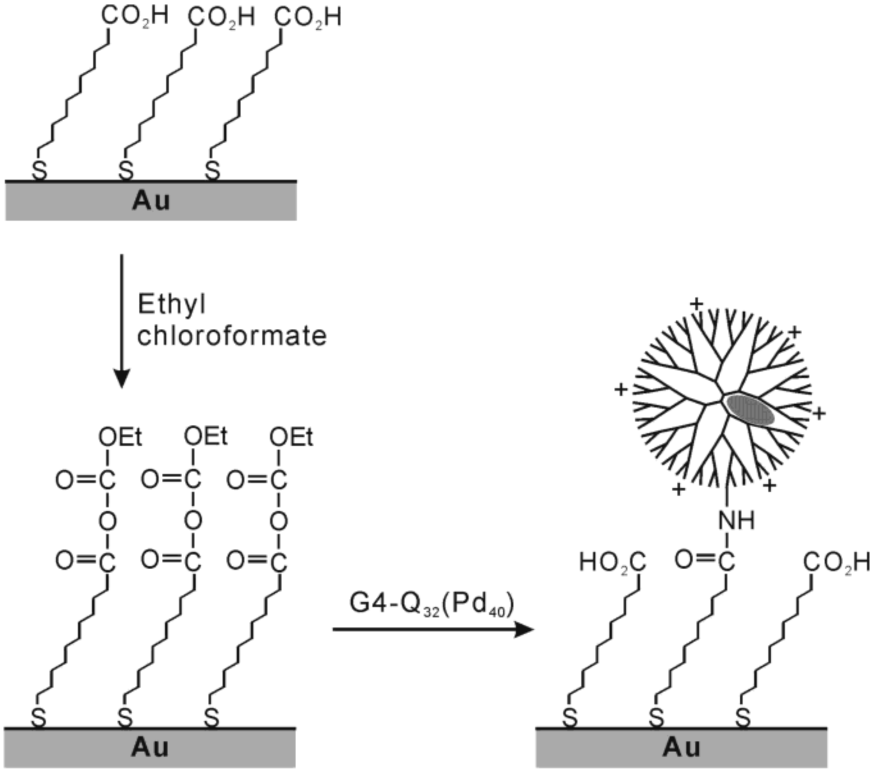


Figure 2. HRTEM images of (a) G4-$Q_{32}(Pd_{40})$ and (c) G4-$Q_{32}(Pt_{40})$ and corresponding particle size distributions of (b) G4-$Q_{32}(Pd_{40})$ and (d) G4-$Q_{32}(Pt_{40})$. The average particle size and distribution were determined by counting 100 metal particles.

Scheme 2



decreases by only ~10% even after 20 successive electrochemical scans between ±0.6 V (vs Ag/AgCl, 3 M NaCl). This level of stability can be compared to our previous results for monolayers of Pt DENs prepared within G*n*-OH dendrimers and physisorbed to Au electrodes.[28] There, we observed that most of the DEN monolayer desorbed after only one voltammetric scan between −0.2 and +0.6 V.[56] We conclude that the enhanced stability here is likely

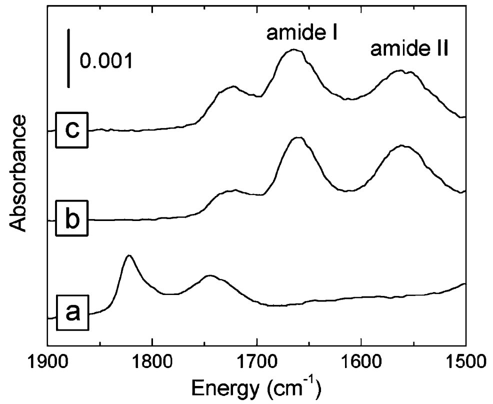


Figure 3. FTIR-ERS spectra of G4-Q_{32}(Pd_{40}) immobilized on anhydride-activated MUA SAMs. (a) An anhydride-activated MUA SAM. (b) A G4-Q_{32}(Pd_{40}) monolayer. (c) A G4-Q_{32}(Pd_{40}) monolayer after 20 continuous electrochemical scans between ±0.6 V (vs Ag/AgCl, 3 M NaCl). Cyclic voltammetric experiments were carried out in an aqueous electrolyte solution of 0.1 M Na_2SO_4 at 100 mV/s.

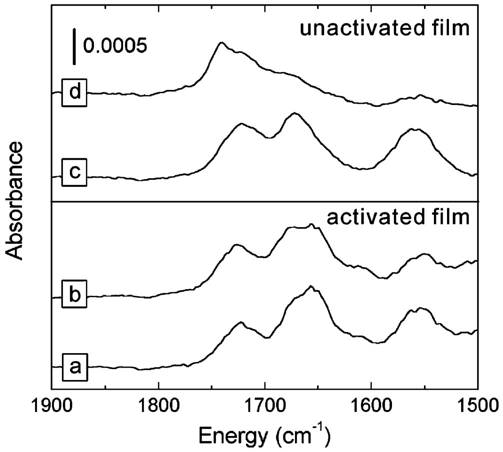


Figure 4. FTIR-ERS spectra of G4-Q_{32}(Pd_{40}) immobilized on (a and b) anhydride-activated MUA SAMs and (c and d) unactivated MUA SAMs (a and c) before and (b and d) after sonication in an aqueous HCl solution (pH = 2.0) for 5 min.

a consequence of the covalent attachment of G4-Q_{32} to the SAM.

In a second set of control experiments, we compared the stability of G4-Q_{32}(Pd_{40}) monolayers immobilized on both unactivated and anhydride-activated MUA SAMs. FTIR-ERS spectra a and b in Figure 4 were obtained from a G4-Q_{32}(Pd_{40}) monolayer on an anhydride-activated MUA SAM before and after, respectively, sonication in an aqueous HCl solution (pH = 2.0) for 5 min. The spectra show that ~85% of the amide band intensities at 1661 and 1560 cm^{-1} remain. In contrast, the intensity of the amide bands of a G4-Q_{32}(Pd_{40}) monolayer prepared on an unactivated MUA SAM (spectrum c in Figure 4) are almost entirely eliminated by the same acid treatment (spectrum d in Figure 4), suggesting that in this case G4-Q_{32}(Pd_{40}) is attached to the surface only by electrostatic interactions between the peripheral cationic groups of G4-Q_{32} and the carboxylate groups of the MUA SAM.

In a third set of control experiments, we compared the stability of a G4-Q_{32} monolayer to that of G4-NH_2 and G4-OH monolayers (Table 1). These data were obtained using metal-free dendrimers. The G4-NH_2 and G4-OH monolayers were prepared using the same activation procedure used for the preparation of the G4-Q_{32} monolayers, and the stability was judged by noting the change in the magnitude of the amide I bands before and after either sonication or electrochemical cycling. For G4-NH_2 monolayers, a high level of stability was observed due to covalent linking of the dendrimer to the MUA SAM via the peripheral primary amine groups.[47,48] Importantly, we found that stability of G4-Q_{32} monolayers is comparable to that observed for G4-NH_2 monolayers. In the case of the G4-OH monolayers, however, 20 successive voltammetric scans results in a ~41% decrease in the intensity of the amide I peak, which reflects poor adhesion of the dendrimer to the SAM. Taken together, these three spectroscopic and stability studies strongly suggest that G4-Q_{32}(Pd_{40}) is covalently linked to the MUA SAM and that this in turn leads to a robust G4-Q_{32}(Pd_{40}) monolayer.

Table 1. Adsorption Stability of G4-Q_{32}, G4-NH_2, and G4-OH Monolayers Immobilized on Anhydride-Activated MUA SAMs

	percentage decrease of amide I peak[a]		
treatment	G4-Q_{32}	G4-NH_2	G4-OH
sonication[b]	0.4	3.0	5.3
sonication + acid[c]	2.3	3.8	62
voltammetric scans[d]	9.0	13	41

[a] The percentage decrease is based on the relative intensity of the amide I peak before and after each treatment. [b] Sonication in H_2O for 5 min. [c] Sonication in an aqueous HCl solution (pH = 2.0) for 5 min. [d] 20 continuous electrochemical scans between ±0.6 V (vs Ag/AgCl, 3 M NaCl). The scan rate was 100 mV/s and the aqueous electrolyte solution contained 0.1 M Na_2SO_4.

Summary and Conclusions

We have described an approach for robust immobilization of DENs on Au surfaces. This was accomplished by encapsulating Pt and Pd nanoparticles within dendrimers having a bifunctionalized periphery and then reacting the dendrimer with an activated SAM. One component of the dendrimer periphery is designed to prevent agglomeration and precipitation during synthesis of the DEN, and the other component is used for linking the DEN to the SAM surface. These findings demonstrate that partially quaternized PAMAM dendrimers are a useful mediator for preparing robust, highly monodisperse metal nanoparticle arrays on surfaces. In a broader sense, it is clear that multiple different functional groups appended onto the periphery of dendrimers can be used to multiplex chemical functionality. This has the potential to be an especially powerful property of dendrimers, because of the very large number of functional groups on their surface. At present we are examining the effectiveness of these surface-immobilized dendrimers for applications in heterogeneous catalysis. The results of those studies will be reported soon.

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Supporting Information Available: ^1H and ^{13}C NMR spectra of G4-Q_{32} and G6-Q_{116}, a MALDI mass spectrum of G4-Q_{32}, and an XPS spectrum of G4-Q_{32}(Pt_{40}) immobilized on an anhydride-activated MUA SAM. This information is available free of charge via the Internet at http://pubs.acs.org.

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