

Preparation of Dendrimer-Encapsulated Metal Nanoparticles Using Organic Solvents

Yanhui Niu and Richard M. Crooks*

Department of Chemistry, Texas A&M University, P.O. Box 30012,
College Station, Texas 77842-3012

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Preparation of dendrimer-encapsulated metal nanoparticles (DEMNs) within amphiphilic dendrimers in an organic solvent is reported. The important new result is that metal ion encapsulation is driven by solubility differences between the metal salt in solution and the dendrimer interior. This contrasts with previous studies, which have relied on specific interactions between metal ions and ligands within the dendrimer interior to drive encapsulation. This new approach makes it possible to prepare relatively large DEMNs. Both Cu and Pd DEMNs have been prepared and the latter are shown to be catalytically active for hydrogenation reactions.

Introduction

We report a new method for preparing dendrimer-encapsulated metal nanoparticles (DEMNs). The significant new finding is that differences in metal-ion solubility between the solvent and the dendrimer interior can be used to drive metal ion encapsulation. Subsequent chemical reduction of the dendrimer/metal ion composite results in formation of DEMNs. This approach contrasts with our previously reported strategy for preparing DEMNs,¹ which relies on specific interactions between metal ions and intradendrimer functional groups for metal-ion encapsulation.^{2,3} Because reliance on specific metal/ligand interactions is relaxed, this new approach provides a means for increasing both the type and size of nanoparticles that can be encapsulated within dendrimers.

Dendrimers are polymers that can be highly monodisperse in size, shape, and chemical composition.^{4–6} We^{1,2} and others^{7–11} have shown that poly(amido amine) (PAMAM) and poly(propylene imine) (PPI) dendrimers can be used as templates for preparing nearly mono-

disperse intradendrimer metal nanoparticles using a “ship-in-a-bottle” approach: first the metal ions are loaded into the dendrimeric template, and then chemical reduction results in formation of DEMNs. Transition metal ions, such as Cu²⁺, Pt²⁺, Pd²⁺, Au³⁺, Ru³⁺, and Ni²⁺, partition into dendrimers from aqueous solutions and complex irreversibly with internal tertiary amine groups. Because the dendrimeric template can be monodisperse in structure, each dendrimer molecule contains about the same number of interior functional groups.^{1,2} Accordingly, the same number of metal ions should reside in each dendrimer, and therefore the intradendrimer nanoparticles that result from reduction should all contain nearly the same number of atoms.

DEMNs are retained within the dendrimer host primarily by steric considerations, but chemical interactions between the dendrimer and metal particle are also probably important. We have previously shown that DEMNs can be rendered soluble in essentially any solvent by controlling the chemistry of their periphery,² that the dendrimeric host can impart selectivity to intrinsically nonselective encapsulated catalytic metal nanoparticles,^{12,13} and that this same synthetic approach can be used to prepare dendrimer-encapsulated semiconductor quantum dots.¹⁴

Nanoparticles soluble in organic solvents can be synthesized by reduction of the corresponding ions in the presence of monomeric amphiphiles such as thiols,^{15,16} micelles,¹⁷ or polymers,^{18,19} or by ligand-ex-

* To whom correspondence should be addressed. Phone: 979-845-5629. Fax: 979-845-1399. E-mail: crooks@tamu.edu.

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change reactions.^{20,21} Dendrimers can also be used to solubilize nanoparticles in nonaqueous solvents. For example, we recently demonstrated that metal particles within water-soluble, amine-terminated PAMAM dendrimers can be transported into an organic phase by addition of a fatty acid.²² It is also possible to extract metal ions from an aqueous phase into a nonaqueous phase,²³ and then reduce the ions to zerovalent metal particles in the nonaqueous phase. Esumi et al.²⁴ were the first to use this approach by preparing dendrimer-encapsulated Au nanoparticles within PAMAM dendrimers carrying hydrophobic groups on their periphery. We later showed that this strategy could also be used to prepare fluorosoluble DEMNs.²⁵ However, the extraction processes was slow and several washing and extraction iterations were required.

Esumi has also demonstrated that it is possible to completely avoid the extraction process and prepare Pt nanoparticles in the absence of water.²⁶ This was accomplished by reduction of PtCl_6^{2-} in ethyl acetate using dimethylamineborane in the presence of methyl-ester-terminated PAMAM dendrimers. This is the approach followed in the present study. Specifically, we modified the periphery of amine-terminated PPI dendrimers with hexanoyl or palmitoyl groups to render them soluble in organic solvents. Next, Cu^{2+} was introduced into the dendrimer by mixing solutions containing CuCl_2 and the dendrimer in a CHCl_3 -MeOH mixed solvent. Finally, DEMNs were obtained by reducing the PPI/ Cu^{2+} composite with NaBH_4 .

In prior studies it was demonstrated that Cu^{2+} does not complex with functional groups inside PPI dendrimers.^{9,27} However, encapsulation of Cu^{2+} is a necessary condition for DEMN formation, and therefore we infer that in our case that metal ions are driven into PPI dendrimers by differential solubility.

Experimental Section

Materials. Poly(propylene imine) dendrimers were purchased from DSM (Geleen, The Netherlands) and were dried under vacuum in a Schlenk flask at 23 ± 2 °C to remove residual H_2O and low-molecular-weight impurities. Palmitoyl chloride, hexanoyl chloride, chloroform (HPLC grade), methanol (HPLC grade), deuterated chloroform, $\text{CuCl}_2 \cdot \text{H}_2\text{O}$, NaBH_4 , and 1-hexene were used as received from the Aldrich Chemical Co. (Milwaukee, WI). Dichloromethane was purchased from Aldrich and distilled over CaH_2 before use. Triethylamine was dried over KOH prior to use. $\text{Pd}(\text{CH}_3\text{CO}_2)_2$ was purchased from Strem Chemicals, Inc. (Newburyport, MA) and used without further purification.

Characterization. ^1H and ^{13}C NMR spectra were recorded on a Unity p300 spectrometer at 300 MHz (75 MHz for ^{13}C). High-resolution transmission electron micrographs (HRTEM) were obtained with a JEOL-2010 TEM having a point-to-point

resolution of 0.19 nm. Samples were prepared by placing a drop of solution on a holey-carbon-coated Au TEM grid and allowing the solvent to evaporate in air. Absorption spectra were recorded on a Hewlett-Packard HP 8453 UV-vis spectrometer. The optical path length was 1.0 or 0.1 cm and the mixed solvent (CHCl_3 -MeOH) was used as reference for all measurements.

Procedure for the Preparation of Hexanoyl or Palmitoyl-Modified Poly(propylene imine) Dendrimers. The procedure used to functionalize the periphery of PPI dendrimers was similar to that reported by Stevelmans et al.²⁸ and Liu et al.²⁹ with minor modifications. For example, a fifth-generation poly(propylene imine) dendrimer having 64 terminal amine groups (D64) was functionalized with palmitoyl (D64P64) as follows. To a solution of 44.9 mg of D64 under N_2 in 20 mL of dry CH_2Cl_2 , 2.5 mL of triethylamine was added, followed by addition of 0.13 mL of palmitoyl chloride (1.1 equiv per terminal amino group). After the mixture was stirred for 15 h at room temperature, the solvent was evaporated. The remaining solid was heated under reflux with 50 mL of diethyl ether for 30 min and filtered to remove the excess palmitoyl chloride. The mixture was then refluxed with saturated aqueous Na_2CO_3 for 6 h followed by extraction with CH_2Cl_2 . The organic layer was separated and dried in vacuo at 23 ± 2 °C to yield a white/yellow solid. Characterization of this material was in accord with results reported by Stevelmans et al.²⁸ Similar procedures were used to prepare the other generations of palmitoyl-functionalized dendrimers (DnPn) and hexanoyl-functionalized dendrimers (DnHn). NMR results for DnHn are given below.

D16H16. ^1H NMR (300 MHz, CDCl_3): δ 0.84 (t, CH_3 , 48H), 1.01–1.69 (m, $\text{CH}_3(\text{CH}_2)_3$, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{N}$, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{NHCO}$, 156H), 2.14 (t, NHCOCH_2 , 32H), 2.34 (m, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{N}$, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{N}$, $\text{CH}_2\text{CH}_2\text{CH}_2\text{NHCO}$, 84H), 3.22 (q, CH_2NHCO , 32H), 7.16 (br, NHCO , 16H). ^{13}C NMR (75 MHz, CDCl_3): δ 14.2, 22.6, 24.9, 25.8, 27.2, 29.9, 31.7, 36.8, 38.0, 51.7, 52.3, 54.4, 174.0.

D32H32. ^1H NMR (300 MHz, CDCl_3): δ 0.85 (t, CH_3 , 96H), 1.16–1.68 (m, $\text{CH}_3(\text{CH}_2)_3$, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{N}$, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{NHCO}$, 316H), 2.15 (t, NHCOCH_2 , 64H), 2.35 (m, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{N}$, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{NHCO}$, 180H), 3.22 (q, CH_2NHCO , 64H), 7.34 (br, NHCO , 32H). ^{13}C NMR (75 MHz, CDCl_3): δ 14.2, 22.7, 24.9, 25.8, 27.3, 29.8, 31.8, 36.8, 38.0, 51.7, 52.4, 174.0.

D64H64. ^1H NMR (300 MHz, CDCl_3): δ 0.86 (t, CH_3 , 192H), 1.19–1.70 (m, $\text{CH}_3(\text{CH}_2)_3$, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{N}$, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{NHCO}$, 444H), 2.17 (t, NHCOCH_2 , 128H), 2.37 (m, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{N}$, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{NHCO}$, 372H), 3.23 (q, CH_2NHCO , 128H), 7.55 (br, NHCO , 64H). ^{13}C NMR (75 MHz, CDCl_3): δ 14.2, 22.6, 24.9, 25.8, 27.2, 29.8, 31.7, 36.8, 38.0, 51.7, 52.3, 174.0.

Procedure for UV-vis Titration of Hexanoyl- or Palmitoyl-Modified PPI Dendrimers with CuCl_2 . UV-vis titrations of the modified dendrimers with Cu^{2+} were carried out to assess the average maximum number of Cu^{2+} ions that can be encapsulated within each dendrimer generation. The titration of D32P32 with Cu^{2+} in $\text{CHCl}_3/\text{MeOH}$ (4:1, v/v) is described as an example. A 1-mL portion of 1×10^{-4} M D32P32 dendrimer CHCl_3 solution was prepared from dry D32P32 and added to a cuvette (optical path, 1 cm) with a cap on the top and a stirring bar at the bottom. CHCl_3 (0.6 mL) and MeOH (0.4 mL) were then added and mixed well to make the $\text{CHCl}_3/\text{MeOH}$ (4:1, v/v) mixed solvent. CuCl_2 (40 mM) in $\text{CHCl}_3/\text{MeOH}$ (4:1, v/v) was added to the stirred dendrimer solution within the cuvette using a micropipet. After addition of an aliquot of the Cu^{2+} solution, the cap was placed on the cuvette to prevent solvent evaporation and then a UV-vis absorption spectrum was obtained.

Preparation of Dendrimer/ Cu^{2+} Complexes and Cu DEMNs. These procedures are described using D32P32(Cu_{40})

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in $\text{CHCl}_3/\text{MeOH}$ (4:1, v/v) as an example. A reaction vial containing a stirring bar was filled with 1 mL of a 1×10^{-4} M DnPn CHCl_3 solution. CHCl_3 (0.6 mL) and MeOH (0.4 mL) were then added and mixed well to make the $\text{CHCl}_3/\text{MeOH}$ (4:1, v/v) mixed solvent. CuCl_2 (100 μL of 40 mM) in $\text{CHCl}_3/\text{MeOH}$ (4:1, v/v) was added to the stirred reaction vial and a yellow solution was obtained. Next, 20 mol equiv of NaBH_4 per metal ion were dissolved in 80 μL of MeOH to which 320 μL of CHCl_3 were added. This solution was then added to the stirred vial to reduce Cu^{2+} to Cu^0 . The color of the solution turned to golden brown. A cap was placed on the container to prevent solvent evaporation. The color of the solution slowly turned yellow in the presence of atmospheric O_2 , but when O_2 was excluded it remained golden brown.

Preparation of Dendrimer/ Pd^{2+} Complexes and Pd DEMNs. These procedures are described using preparation of $\text{D32P32}(\text{Pd}^{2+})_{20}$ and $\text{D32P32}(\text{Pd})_{20}$ as an example. A 1×10^{-4} M D32P32 solution (300 μL) in $\text{CHCl}_3/\text{MeOH}$ (2:1, v/v) was placed in a reaction vial. CHCl_3 (1640 μL) and MeOH (955 μL) were then added and mixed well to make the $\text{CHCl}_3/\text{MeOH}$ (2:1, v/v) mixed solvent. With vigorous stirring, 15 μL of 40 mM $\text{Pd}(\text{OAc})_2$ in MeOH was added. A cap was placed on top of the vial to prevent solvent evaporation. After stirring for 30 min, 20 equiv of NaBH_4 in $\text{CHCl}_3/\text{MeOH}$ (2:1, v/v) were added dropwise to the vial to yield golden brown $\text{D32P32}(\text{Pd})_{20}$.

Hydrogenation Reactions. The hydrogenation apparatus was the same as that described in ref 13. To a 25-mL Schlenk flask, 300 μL of a 1×10^{-4} M D32P32 solution in $\text{CHCl}_3/\text{MeOH}$ (2:1, v/v), 1640 μL of CHCl_3 , and 955 μL of MeOH were added and mixed well, followed by addition of 15 μL of 40 mM $\text{Pd}(\text{OAc})_2$ in MeOH under vigorous stirring. A light yellow solution was obtained immediately. After stirring for 30 min, 90 μL of a 133 mM NaBH_4 $\text{CHCl}_3/\text{MeOH}$ (2:1, v/v) solution was added, which changed the color of the solution to golden brown. All the joints of the apparatus were sealed with silicone grease and checked for leaks before adding the substrate. The system was purged with H_2 for 15 min with continuous addition of $\text{CHCl}_3/\text{MeOH}$ (2:1, v/v) to maintain the volume. To verify that H_2 was not consumed in the absence of substrate, the catalyst was stirred in solution over a known volume of H_2 . The H_2 volume did not change over a period of hours. Experiments were carried out by adding 0.6 mmol 1-hexene by syringe under vigorous stirring conditions. The rate of stirring was maintained high and constant throughout all hydrogenation reactions.

Results and Discussion

General Approach. We^{1,2} and others^{7,8,10,11} have previously shown that reduction of metal ions specifically coordinated to ligand sites within dendrimers present in aqueous solutions leads to formation of dendrimer-encapsulated metal nanoparticles.^{2,3} Although this synthetic approach is broadly applicable, we sought to further generalize it. The approach is to use solubility differences between the solvent and the dendrimer interior to drive the encapsulation process, rather than relying exclusively on fixed stoichiometries between metal ions and ligands. This new approach eliminates the size limitation imposed on DEMNs by the finite number of ligand sites within dendrimers. We wish to emphasize that Esumi et al. have previously used methyl-ester-terminated dendrimers to prepare Pt DEMNs using ethyl acetate as the solvent. However, the role played by differential solubility was not examined in that study.²⁶

To test this new synthetic approach we synthesized and characterized hydrophobic PPI dendrimers terminated on their periphery with either palmitoyl (C16) (DnPn, $n = 16, 32,$ and 64) or hexanoyl (C6) (DnHn, $n = 16, 32, 64$) functional groups.^{28,29} Longer (C16) and

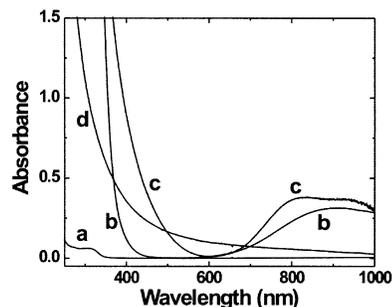


Figure 1. Absorption spectra of $\text{CHCl}_3/\text{MeOH}$ (4:1, v/v) solutions containing: (a) 0.050 mM D32P32 ; (b) 2.0 mM CuCl_2 ; (c) 0.050 mM D32P32 and 2.0 mM CuCl_2 ; and (d) $\text{D32P32}(\text{Cu}_{40})$. The optical path length was 1 cm and the temperature was 25 ± 2 °C.

shorter (C6) alkyl chain-lengths were used to determine if the hydrocarbon periphery plays a role in controlling nanoparticle size. CHCl_3 -MeOH is a miscible mixed-solvent system in which both dendrimers and metals ions are soluble. This is a convenience that avoids the extra step of a biphasic extraction of the metal into the dendrimers. This mixed solvent also makes it possible to use CuCl_2 rather than more hydrophobic salts, such as $\text{Cu}(\text{OAc})_2$, which have less desirable spectroscopic properties.³⁰

Dendrimer-Encapsulated Cu Nanoparticles. Encapsulated Cu nanoparticles were synthesized by first introducing Cu^{2+} into the dendrimer interior and then chemically reducing the resulting nanocomposite.^{1,2} To characterize each stage of the synthesis leading up to formation of the DEMNs we monitored the relevant solutions by UV-vis absorption spectroscopy (Figure 1). In the absence of Cu^{2+} , dendrimer D32P32 does not absorb light in the range of 350–1000 nm, whereas Cu^{2+} alone in the mixed solvent reveals a broad absorption centered around 900 nm corresponding to the $d-d$ transition of Cu^{2+} . In the presence of both Cu^{2+} and D32P32 ($[\text{Cu}^{2+}]/[\text{D32P32}] = 40$) the solution turns yellow, the absorption maximum shifts to 835 nm, and the extinction coefficient at 835 nm increases by 40% (spectrum c, Figure 1). In contrast, aqueous or methanolic solutions of dendrimer/ Cu^{2+} nanocomposites are usually blue and exhibit a $d-d$ transition around 600 nm^1 or 620 nm^{27} .

NaBH_4 is not very soluble in CHCl_3 . However, by first dissolving NaBH_4 in MeOH and then adding CHCl_3 , it is possible to prepare a 200 mM solution of NaBH_4 in $\text{CHCl}_3/\text{MeOH}$ (4:1, v/v). Upon the addition of NaBH_4 , the dendrimer-containing solution turns brown and the discrete $d-d$ transition resulting from Cu^{2+} is replaced by a monotonically increasing absorption to shorter wavelength (spectrum d, Figure 1). This indicates conversion of Cu^{2+} to zerovalent Cu nanoparticles.³¹ When the same experiment is carried out in the absence of dendrimer, Cu^0 precipitates as soon as NaBH_4 is introduced. This suggests stabilization of the nanoparticle by the hydrophobic dendrimer. If the D32P32 -encapsulated Cu^0 composite is exposed to atmospheric O_2 for 4 h, then the Cu^0 nanoparticles start to reoxidize

(30) $\text{Cu}(\text{OAc})_2$ and related complexes were avoided in this study because their $d-d$ transitions are too close to where the $\text{Cu}-\text{N}$ $d-d$ transition occurs.

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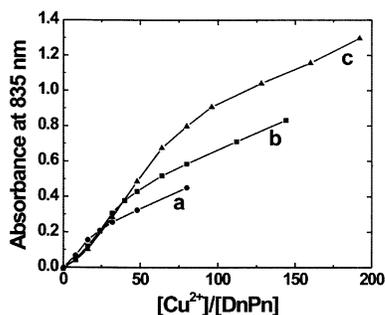


Figure 2. Spectrophotometric titration curves recorded at $\lambda_{\max} = 835$ nm for different ratios of $[\text{Cu}^{2+}]$ and $[\text{DnPn}]$ for (a) D16P16, (b) D32P32, and (c) D64P64. The initial concentration of each dendrimer was 0.050 mM. The optical path length was 1 cm, the temperature was 25 ± 2 °C, and the solvent was $\text{CHCl}_3/\text{MeOH}$ (4:1, v/v).

and the solution color changes from golden brown back to yellow. This reduction–oxidation cycle can be repeated many times.

Determination of the Maximum Cu^{2+} Loading of DnPn Dendrimers. Figure 2 shows the results of a titration of D32P32 dendrimers with a 40 mM CuCl_2 solution in $\text{CHCl}_3/\text{MeOH}$ (4:1, v/v). The titrations were carried out by mixing discrete ratios of DnPn with Cu^{2+} , adjusting the total volume of the solution, and measuring the absorbance at $\lambda_{\max} = 835$ nm. We have previously shown that titrations carried out in this way using hydroxyl-terminated PAMAM dendrimers lead to plots having two distinct linear regions.¹ In those studies we associated the point defined by extrapolation of these two linear regions as an estimate of the maximum number of Cu^{2+} ions residing within the dendrimers. In the present case, this analysis suggests maximum ratios of $[\text{Cu}^{2+}]/[\text{DnPn}]$ of 20 ± 2 , 40 ± 3 , and 75 ± 3 for D16P16, D32P32, and D64P64, respectively. The initial slope of the titrations shown in Figure 2 indicate that the extinction coefficients for Cu^{2+} associated with DnPn is $\epsilon_1 \sim 180 \text{ M}^{-1} \text{ cm}^{-1}$. The slope after the threshold ($\epsilon_2 \sim 90 \text{ M}^{-1} \text{ cm}^{-1}$) is significantly smaller. The titrations were terminated at a ratio of Cu^{2+} to dendrimer about twice that of the threshold value, because in preliminary studies no further change in slope was observed.

The threshold numbers determined here are substantially higher than the corresponding maximum complexation numbers for both PPI/ Cu^{2+} and PAMAM/ Cu^{2+} composites, which arise exclusively from specific interactions between nitrogen-containing ligands and Cu^{2+} in methanolic or aqueous solutions, respectively.^{1,9,27} In the PPI/ Cu^{2+} case, Bosman et al.²⁷ and Floriano et al.⁹ demonstrated that Cu^{2+} only coordinates with peripheral primary amines and the outermost tertiary amines but not interior tertiary amines. In our experiment, after functionalization of the surface of the PPI dendrimer with alkyl groups, there are only two types of nitrogens present: interior tertiary amines and amides. Accordingly, it does not seem likely that strong, specific interactions between Cu^{2+} and interior ligands are responsible for encapsulation. However, to test the importance of interactions between amides and Cu^{2+} , *N,N*-hexamethylenediacetamide was mixed with Cu^{2+} in $\text{CHCl}_3/\text{MeOH}$. No shift in λ_{\max} was observed and addition of NaBH_4 caused immediate precipitation, which indicates little or no coordination of Cu^{2+} with the amide ligand. Additionally, the titration threshold

numbers (D16P16, 20 ± 2 ; D32P32, 40 ± 3 ; and D64P64, 75 ± 5) are significantly larger than the number of tertiary amines within these dendrimers (14, 30, and 62, respectively). Finally, we have previously shown that coordination between Cu^{2+} and tertiary amines in PAMAM dendrimers is actually substoichiometric ($[\text{Cu}^{2+}]/[\text{tertiary amines}] = 0.25$ for hydroxyl-terminated G4 PAMAM dendrimers). On the basis of these arguments, we conclude that the high concentration of Cu^{2+} associated with DnPn dendrimers is primarily due to differential solubility of the metal ion in the dendrimer interior versus in the solvent.

A control experiment showed that in the absence of dendrimer, the extinction coefficient of CuCl_2 in $\text{CHCl}_3/\text{MeOH}$ (4:1, v/v) ($\epsilon \sim 130 \text{ M}^{-1} \text{ cm}^{-1}$) is much larger than ϵ_2 . That is, after the threshold is attained for Cu^{2+} encapsulation in DnPn, the excess metal does not exist as free Cu^{2+} . The value of ϵ_2 is also independent of dendrimer generation. We conclude that prior to the encapsulation threshold Cu^{2+} is strongly associated with the dendrimer and after the threshold it is still associated, but more weakly so. This difference in the chemical environment of the metal ions accounts for the difference in the numerical values of ϵ_1 and ϵ_2 . This conclusion is supported by the finding that reduction of solutions in which the $[\text{Cu}^{2+}]/[\text{DnPn}]$ ratio is less than the threshold value results in soluble DEMNs, whereas ratios exceeding the threshold lead to immediate metal precipitation.

Similar experiments employing DnHn dendrimers yield nearly identical results. That is, the extinction coefficients for Cu^{2+} complexed with DnHn before the threshold is $\sim 170 \text{ M}^{-1} \text{ cm}^{-1}$, and the slope after the threshold is $\sim 90 \text{ M}^{-1} \text{ cm}^{-1}$. This indicates that the length of the alkyl chain (>6 carbon atoms) appended to the periphery of PPI dendrimers does not substantially influence encapsulation of Cu^{2+} .

Although the exact nature and location of the loosely associated Cu^{2+} is unknown at this time, it is clear that a relatively large amount of Cu^{2+} is driven into the dendrimer by differential solubility below the threshold value and that it can be reduced to yield stable DEMNs.^{7–11} Because of the aforementioned air oxidation of Cu, and because of their poor contrast in TEM, it was not possible to obtain good micrographs of Cu DEMNs.

Dendrimer-encapsulated Pd nanoparticles can be synthesized using the approach just described for Cu DEMNs. These experiments were carried out by adding $\text{Pd}(\text{OAc})_2$ to a $\text{CHCl}_3/\text{MeOH}$ (2:1, v/v) solution of DnPn. Here, $\text{CHCl}_3/\text{MeOH}$ (2:1, v/v) was used as the solvent because a Pd precipitate was obtained when NaBH_4 was added to the D32P32/ Pd^{2+} complex in 4:1 $\text{CHCl}_3/\text{MeOH}$. Prior to reduction this solution was yellow, but a clear golden brown solution was obtained following reduction by NaBH_4 . The absorption spectra of D32P32(Pd^{2+})₂₀ and D32P32(Pd_{20}) (Figure 3) are consistent with formation of Pd DEMNs.¹² XPS analysis of the Pd DEMNs confirms the presence of Pd^0 (Supporting Information). The Pd DEMNs were analyzed by HRTEM and found to have a size of 2.3 ± 0.2 nm (Figure 4). Currently we do not understand why the sizes of these particles are larger than the value calculated for a 20-atom crystal (0.9 nm).³² However, our group^{2,12,13,33} and others^{9,34}

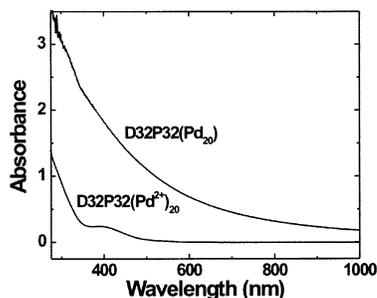


Figure 3. Absorption spectra for 0.050 mM D32P32(Pd²⁺)₂₀ and D32P32(Pd₂₀) in CHCl₃/MeOH (2:1, v/v). The optical path length was 0.1 cm and the temperature was 25 ± 2 °C.

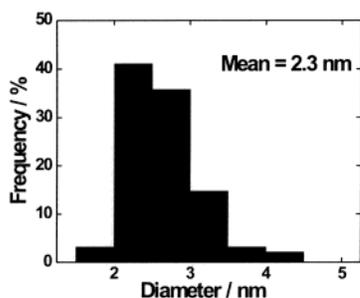
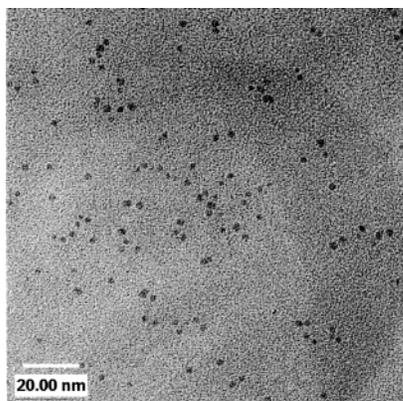


Figure 4. TEM images and particle size distributions for D32P32(Pd₂₀).

have previously observed larger-than-anticipated particle sizes for certain combinations of dendrimers and metals. We believe this difference may result from particles having complex shapes that are most easily accommodated by the restricted volume of the dendrimer interior.

Because these dendrimer-encapsulated Pd nanoparticles are hydrophobic, they can be used for catalysis in organic solvents. For example, the rate of hydrogenation for 1-hexene in the presence of the D32P32(Pd₂₀) catalyst was determined by H₂ uptake.¹³ The initial turnover frequencies in CHCl₃/MeOH (2:1, v/v) for this substrate was 120 mol H₂(mol Pd)⁻¹ h⁻¹. This rate is

(32) The size of a spheroidal particle containing 20 close-packed Pd atoms should be 0.9 nm in diameter.

(33) Zhao, M.; Crooks, R. M. *Adv. Mater.* **1999**, *11*, 217–220.

(34) Li, Y.; El-Sayed, M. A. *J. Phys. Chem. B* **2001**, *105*, 8938–8943.

about the same as that reported for polymer-supported Pd⁰ catalysts.³⁵ However, in contrast to PAMAM-based DEMNs, the modified PPI dendrimer-encapsulated Pd nanoparticles precipitate after about 20 min under hydrogenation conditions.^{12,13,33} The underlying reason for the poor stability is not understood at this time.

Summary and Conclusions

The important result of this study is that solubility differences between metal ions in solution and within dendrimers can be used to drive encapsulation. Although the dielectric constant of dendrimer interiors has not been definitively measured, we estimate the value is somewhat less than 23.³⁶ The estimated dielectric constant of the mixed solvent systems is 10.³⁷ It is this difference in dielectric constant that we believe to be responsible for metal ion encapsulation under the conditions used in this study.

The encapsulation approach described here complements our previous discovery that functional groups within dendrimers can be used as metal-ion templates for the formation of DEMNs.^{1,2} The results of this new study indicate that the main function of the alkyl groups on the modified PPI dendrimers is simply to solubilize the dendrimer. However, they may also weakly associate with metal ions in a way that we do not understand at this time. This method is sufficiently versatile that both Pd and Cu DEMNs can be synthesized. Pd DEMNs prepared using this method are catalytically active, but they are significantly less stable than DEMNs prepared by other routes.

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Supporting Information Available: XPS spectrum of D32P32(Pd₂₀) (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(35) Selvaraj, P. C.; Mahadevan, V. *J. Polym. Sci. Part A: Polym. Chem.* **1997**, *35*, 105.

(36) Because no reference is available for the dielectric constant values of poly(propylene imine) dendrimers, the value quoted here is an estimated value for a G2-NH₂ PAMAM dendrimer which can be inferred from a study using a fluorescent pyrene probe: Pistolis, G.; Malliaris, A.; Paleos, C. M.; Tsiourvas, D. *Langmuir* **1997**, *13*, 5870–5875. An alternative probe has also been used to study the PAMAM interior up to G8 generation, but the interior dielectric constant is not quantified: Richter-Egger, D. L.; Landry, J. C.; Tesfai, A.; Tucker, S. A. *J. Phys. Chem. A* **2001**, *105*, 6826–6833.

(37) Dielectric properties of mixed solvents are in general not equal to the fractional sum of the dielectric constants of each component. However, as a first approximation, we assume the final dielectric constant of the CHCl₃/MeOH solvents is a linear combination of the dielectric constants of two solvents, taking into account relative mole fractions. The dielectric constants of CHCl₃ and MeOH are 4.8 and 32.6, respectively.