

Self-Assembled Inverted Micelles Prepared from a Dendrimer Template: Phase Transfer of Encapsulated Guests

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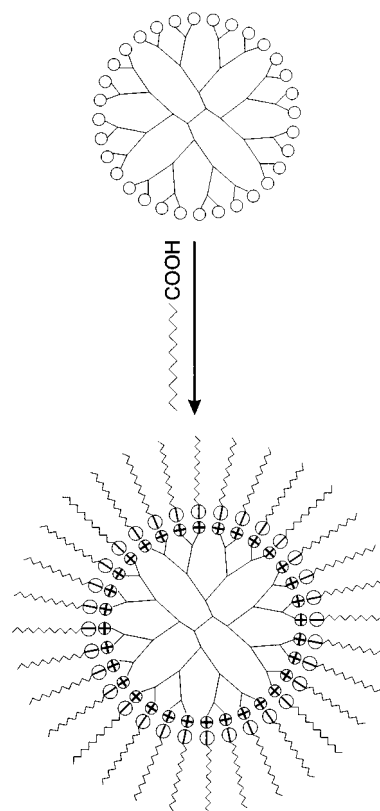
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Here we describe the spontaneous assembly of fatty acids onto the surface of amine-terminated, poly(amidoamine) (PAMAM) dendrimers (Scheme 1). This process, which is driven by acid–base chemistry and ion pairing, results in the extraction of dendrimers from aqueous solutions to nonpolar phases. Dendrimer-encapsulated guest molecules, such as the hydrophilic dyes and catalytically active metal nanoparticles described here, can thus be easily solubilized in organic solvents.

Dendrimers are monodisperse, hyperbranched polymers possessing a very high concentration of surface functional groups.¹ Many of the properties of dendrimers, including their solubility, are strongly influenced by the nature of these terminal functionalities.^{2,3} For example, dendrimers terminated in hydrophobic groups are soluble in nonpolar solvents, while those having hydrophilic groups are soluble in polar solvents such as water and low-molecular-weight alcohols.^{4–6} Terminal groups are normally covalently bonded to the body of dendrimers, but there have been a few reports of electrostatic binding of charged molecules to the surface of dendrimer polyions.^{1,7–10} We now demonstrate that complete surface modification of dendrimers can be accomplished by spontaneous, acid–base self-assembly, which eliminates the need for chemical synthesis and purification. A similar approach has previously been reported for solubilization of ionic polymers^{11,12} and DNA^{13,14} in organic solvents. The electrostatic self-assembly process we report is reversible, and therefore the dendrimers and whatever guests they may contain can be easily shuttled between hydrophilic and hydrophobic phases by adjustment of the pH of the aqueous phase.

Fourth-generation, amine-terminated PAMAM dendrimers (G4-NH₂) readily dissolve in toluene or heptane containing dodecanoic acid. The amount of G4-NH₂ that can be dissolved in 1% dodecanoic acid/toluene corresponds to about 1 dendrimer per

Scheme 1



70–80 molecules of acid¹⁵ which suggests an approximately 1:1 stoichiometry between the fatty acid and each of the 64 terminal amine groups present on the dendrimers. Transmission FT-IR spectroscopy of this toluene solution (Figure 1) indicates that solubilization is accompanied by proton transfer from the acid to the terminal amine groups of the dendrimers and that ionization is essentially complete. Evidence for this comes from the nearly complete disappearance of the dodecanoic acid carboxyl peak at 1710 cm⁻¹ (part a of Figure 1) and the appearance of the asymmetric carboxylate peak at 1557 cm⁻¹ (part c of Figure 1) upon addition of dendrimer.¹⁶ We conclude that the acid molecules arrange themselves around the dendrimer in a composite structure that resembles an inverted micelle having a hydrophilic dendritic interior and a hydrophobic alkyl-chain-dominated exterior that lends solubility to the ensemble (Scheme 1). In the presence of large excesses of dodecanoic acid, proton transfer extends to the tertiary amine groups within the dendrimer interior (see Supporting Information).

Dendrimers with covalently grafted hydrophobic terminal groups have previously been shown to dissolve in nonpolar solvents and solubilize encapsulated guest molecules.^{3,4,6} The present system, however, offers two significant advantages. First, commercially available dendrimers can be used directly to prepare solutions in nonpolar solvents without the need for chemical synthesis or separation. Second, since acid–base interactions are reversible, addition of HCl to the aqueous phase or simple dilution of the organic phase with pure solvent leads to the transfer of G4-NH₂ back into aqueous layer. We report here two examples

(15) This value was calculated from the maximum amount of neat G4-NH₂ which completely dissolves in 1% dodecanoic acid/toluene mixture after 5 min of sonication.

(16) The $\nu_a(\text{CO}_2^-)$ peak at 1557 cm⁻¹ overlaps with the amide II band. In a similar system with the PAMAM dendrimer replaced by a poly(propyleneimine) Cascade dendrimer which does not contain any amide bonds, we have clearly observed the appearance of the $\nu_a(\text{CO}_2^-)$ peak.

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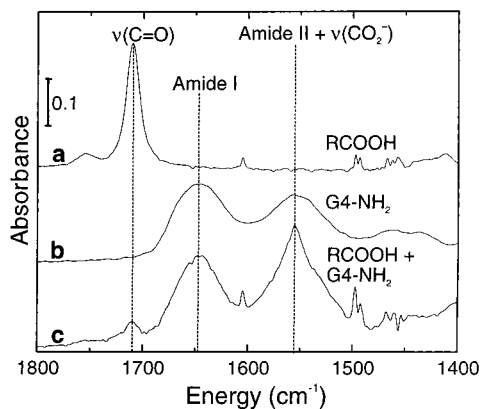


Figure 1. Transmission FT-IR spectra of (a) a 1% dodecanoic acid/toluene mixture, (b) neat G4-NH₂, (c) a G4-NH₂ solution in 1% dodecanoic acid/toluene (the molar ratio of primary amine groups/dodecanoic acid is 0.75). Spectra (a) and (c) were recorded in a solution cell (optical path length 0.05 mm). Spectrum (b) was recorded as a neat film and therefore has an arbitrary scale.

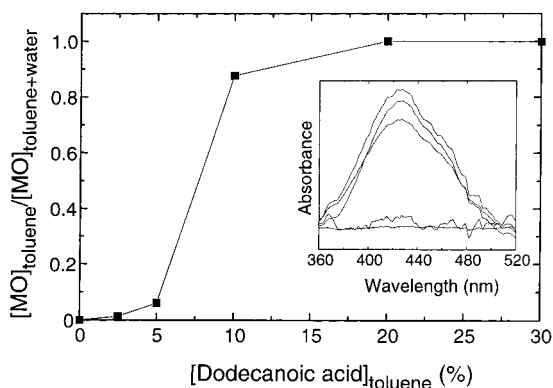


Figure 2. A plot illustrating the partitioning of methyl orange (MO) between an aqueous dendrimer solution and toluene containing various amounts of dodecanoic acid. The initial concentrations of dendrimer and MO in the aqueous layer were 360 and 4 μ M, respectively. The inset shows the UV-vis spectra of the corresponding toluene layers.

of how the G4-NH₂/dodecanoic acid system can be used as a phase-transfer vehicle: transport of methyl orange dye into toluene and preparation of stable toluene solutions of catalytically active Pd nanoparticles.

Methyl orange is a hydrophilic organic dye capable of binding to amine groups in supramolecular structures.^{3,17} Using UV-vis spectroscopy, we monitored the extent to which the dendritic micelles transferred the dye from an aqueous dendrimer solution to toluene containing dodecanoic acid. The results (Figure 2) show that the dye is almost quantitatively transported into toluene containing >10% dodecanoic acid.¹⁸

We previously reported that dendrimer-encapsulated metal nanoparticles could be prepared by sorption of metal ions into the interior of hydroxyl-terminated dendrimers, followed by chemical reduction.¹⁹ Using a similar approach, we are now able to prepare Pd nanoparticles within NH₂-terminated dendrimers.²⁰

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These nanocomposites can be quantitatively transported from the aqueous phase into toluene containing 10–20% of dodecanoic acid.²¹ The transition is readily visualized by the color change: the brown aqueous solution of dendrimer-encapsulated Pd nanoparticles becomes clear after addition of the acid, while the toluene layer turns brown. Neat G4-NH₂/Pd nanocomposites, prepared by dialysis of the crude, postreduction reaction mixture, followed by rotary evaporation at 20 °C, can also be dissolved in toluene containing slightly more than a stoichiometric amount of dodecanoic acid.

Toluene solutions of dendrimer-encapsulated Pd nanoparticles were tested for catalytic activity by examining their effectiveness toward hydrogenation.²² Dodecanoic acid (2% w/w) was used to effect solubilization of the G4-NH₂/Pd composite in the organic phase. The concentration of the substrate (allyl alcohol) was 0.4 M and the concentration of the Pd catalyst (based on the number of Pd atoms) was 0.2 mM. The reaction product was confirmed to be 1-propanol by ¹H NMR spectroscopy, and the turn-over frequency, calculated from the rate of hydrogen uptake, was ~ 760 mol H₂ (mol Pd)⁻¹ h⁻¹ at 20 °C. This value compares favorably with the value of 218 mol H₂ (mol Pd)⁻¹ h⁻¹ reported for the same reaction in water catalyzed by similarly prepared Pd particles encapsulated in OH-terminated dendrimers.²²

In conclusion, we have described a simple, noncovalent means for converting dendrimer exteriors from hydrophilic (-NH₂) to hydrophobic. The method is based on the formation of ion pairs between fatty acids and the terminal amine groups of dendrimers, and it leads to the formation of toluene-soluble, inverted micelle-like structures. These materials are extracted into nonpolar solvents from aqueous phases and can transport hydrophilic guest molecules with them. Such composites are especially well-suited for solubilization of catalytically active metal nanoparticles in nonpolar solvents. The reversible nature of dendrimer/acid interactions makes it possible to extract the catalyst back into aqueous phase at pH 2. The catalyst can then be dissolved again in toluene/dodecanoic acid mixture after dialysis and rotary evaporation.

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Supporting Information Available: A plot of the total number of dodecanoate ions coordinated to each dendrimer as a function of the dodecanoic acid/dendrimer molar ratio in toluene (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(20) Pd nanoparticles were prepared by reducing aqueous K₂PdCl₄ with NaBH₄ in the presence of G4 PAMAM dendrimers. The Pd/dendrimer molar ratio was 10/1. To prevent coordination of Pd²⁺ to the primary amine groups of G4 dendrimer, the pH of dendrimer solution was adjusted to ca. 2, which preferentially protonates the exterior amines to a greater extent than the less basic interior tertiary amines (Tomalia, D. A.; Naylor, A. M.; Goddard, W. A. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 138). Accordingly, Pd²⁺ binds preferentially to the interior tertiary amines and upon reduction Pd particles form within the dendrimer interior. After the reduction was complete (10 min), the pH of solutions was adjusted back to ca. 8.5.

(21) Only freshly prepared Pd/G4-NH₂ nanocomposites can be extracted into the toluene layer: particles stored for more than 16 h can only be dissolved in toluene after dialysis followed by rotary evaporation (vide supra).

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