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Poly(Amidoamine) Dendrimer-Templated Nanocomposites. 1. Synthesis of Zerovalent Copper Nanoclusters

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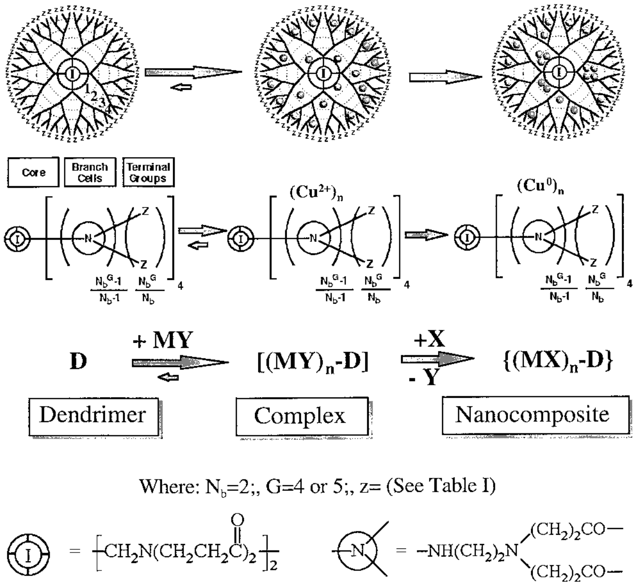
Preparations of stable metallic copper(0) solutions have been demonstrated. After complexation within various surface modified poly(amidoamine) (PAMAM) dendrimers, copper(II) ions were reduced to zerovalent copper thus providing a dendrimer−metal nanocomposite. Solubility of the metal domains is determined by the surface properties of the host dendrimer molecules; however, their solutions still display characteristic optical properties associated with metal domains. Both aqueous and methanolic solutions of copper clusters were stable for several months in the absence of oxygen.

The ability to construct nanoscale objects in unlimited quantities is presently an ultimate challenge in contemporary materials research.[1−4] Nanoscale, zerovalent metal clusters with a high level of size/structure control would be of significant interest for use in catalysis,[5a,b] optoelectronics,[6] or other nano-devices.[7]

Recently, we reported a very versatile method for producing dendrimer nanocomposites which involves the assembly of inorganic compounds within the interiors of dendrimers.[8] Dendrimers are monodispersed nanoreactors,[9−12] possessing architectures[13−16] and ligand sites that allow the preorganization of metal ions[15] within their interiors. Use of PAMAM[13] dendrimers as template/container molecules[16,17] (see Scheme 1, Table 1) allows "*in situ*" generated reaction products to be dispersed as amorphous or slightly ordered domains at the atomic/molecular level within the dendrimer interior; wherein, the branch cells may act as separators.[19] Several application areas are being explored in our laboratories including semiconductors,[8] noble metals,[20a] environmental cleanup,[20b] magnetic dendrimer nanocomposites[20c] and catalysts.[20d]

Scheme 1. Construction of Dendrimer Nanocomposites[a]



[a] Y are the ligands before complex formation and X are the ligands in the nanocomposite, provided by a second reactant. Note, that X may be missing in the case of zero valence metals.

Copper ions were chosen to demonstrate this novel concept, since their oxidation and spectral properties have been extensively investigated.[21a] Furthermore, copper complexation properties of PAMAM dendrimers have been extensively examined.[12,21b,24,25] Alcohols, hydrazine, sodium borohydride, or sodium citrate[22] have been traditionally used to make metal nanoclusters.[18,22] It is well-known, however, that copper nanoclusters tend to aggregate very quickly.[23]

Utilizing the same reducing agents on dendrimer complexes, we have observed nanocomposite formations with unprecedented stability both in water and methanol. For example, aqueous solutions of {$Cu(0)_n$−PAMAM} dendrimer−copper nanocomposites (i.e., metallic copper domains synthesized in PAMAM dendrimers) have been stored for *more than 90 days at room temperature and found to be stable in the absence of oxygen.*

Thus, a typical procedure may be described as follows: to a 1 mL solution of G4.0 PAMAM (1×10^{-6} mol, 14.215 mg) dendrimer was added 1 mL of 10 mM copper(II) acetate solution (1.99 mg, 1×10^{-5} mol). The Cu^{2+} ion complexing capacity of a particular PAMAM dendrimer was followed by spectrophotometric titrations (Figure 1). By titrating the dendrimer solutions

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Table 1: Comparison of PAMAM Dendrimers Used

notation	terminal z-groups	no. of 3°-N branch cells	no. of 3°-N and 1°-N ligands[a]	no. of metal sites[b]	possible metal regios
G4.T (TRIS)	64 each $-NHC(CH_2OH)_3$	62	62	15.5	interior
G4.0 (amino-surface)	64 each $-NH(CH_2)_2NH_2$	62	126	31.5	interior and exterior
G5.P (pivalate)	128 each $-NH(CH_2)_2NHCO(CH_3)_3$	126	126	31.5	interior

[a] Note: a generation 2 *tris*-(2-hydroxymethyl)methyl surface aliphatic polyether dendrimer was also tested and did not cause any comparable spectral change when mixed with the aqueous solution of Cu^{2+}. [b] Calculated number of maximum possible copper ions assuming tetracoordination.

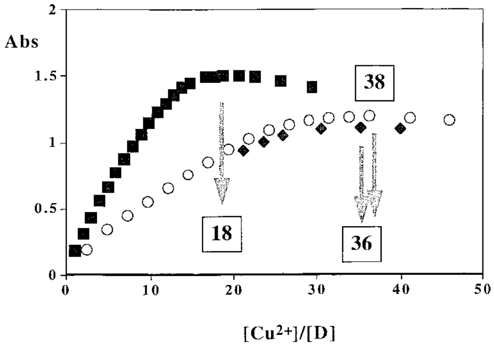

Figure 1. Comparison of UV−vis absorption curves for $[(Cu(Ac_2)_n-$PAMAM_G4.T] (■ at 299 nm, $[(Cu(Ac_2)_n-$PAMAM_G4.0] (◆ at 270 nm), and $[(Cu(Ac_2)_n-$PAMAM_G5.P] (○ at 282 nm) as measured at the wavelength of their characteristic metal−ligand absorption bands as a function of copper ion-to-dendrimer ratio. D = dendrimers. Determination of capacity was based on the highest achieved maximum absorbance.

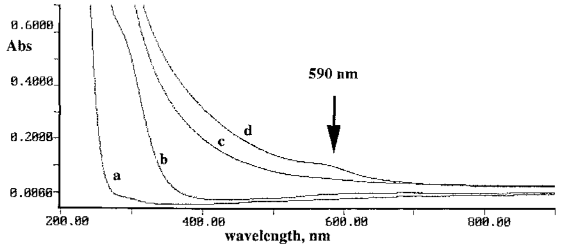

Figure 2. UV−visible spectra of the host dendrimer (a) and of the $\{Cu(0)_{10}$-G4.T} nanocomposite solution after 1 min (b), 2 h (c), and 21 h (d) after reduction by hydrazine.

with aqueous Cu-acetate it was possible to load the dendrimer hosts to various metal levels. Metal levels were assayed by both atomic absorption spectroscopy and UV−vis spectral analysis.

Reduction without dendrimers resulted in copper-colored macroscopic particles or partial deposition of copper-mirrors on the wall of the vials. A typical reduction involved the dropwise addition of 10 μL aqueous hydrazine (30% solution, 3 mg, 1×10^{-4} mol) by means of a microsyringe to the $[(CuAc_2)_{10}-$PAMAM_G 4.0] complex solution while vigorously stirring. An immediate loss of dark blue color with concurrent formation of light yellow solutions was observed.

UV−visible absorption of the hydroxyl-terminated $\{(CuAc_2)_{10}-$PAMAM_G4.T} nanocomposite manifested an annealing event; wherein, after 21 h a plasmon peak appeared at 590 nm on the exponential curve and very slowly increased with time (Figure 2). Samples of $\{(CuAc_2)_{10}-$PAMAM_G4.0} and $\{(CuAc_2)_{27}-$PAMAM_G5.P} remained unaggregated at 0.3−0.1% concentration for more than 90 days at room temperature. Exposure to atmospheric oxygen caused oxidation through a green Cu(I) complex back to Cu^{2+}complexes, thus indicating catalytic activity.

All three nanocomposite solutions displayed strong UV−vis absorption at very short wavelengths thus suggesting the presence of separated copper atoms or very small copper domains (see Figure 3). Depending on the polarity of the dendrimer surface substituents, the metallic component may be directed[20a] primarily near the dendrimer surface or deeper into the interior.

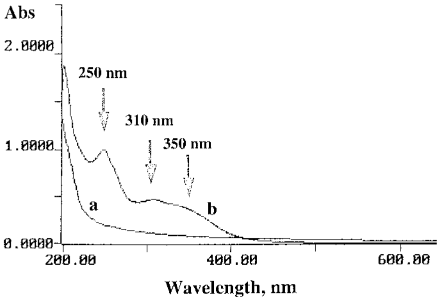

Figure 3. Comparison of UV−visible spectra of the $\{Cu(0)_{27}-$PAMAM_G5.P} nanocomposite (0.25 mM) and PAMAM_G5.P (0.25 mM) in methanol.

These shortwavelength positions are determined by free electrons.[26] Other than the nanocomposites, only PAMAM and hydrazine were present in the water or methanol solvents. The presence of hydrazine makes oxidation to aminoxides improbable; therefore, we believe these bands are due to copper domains dispersed within the dendrimers. UV photoelectronic spectra for small$(Cu(0))_n$ copper clusters have been reported.[27,28]

According to optical absorption theory, uniform spheres that are much smaller than the wavelength of light[26,29] produce a plasma absorption band for copper at 590 nm if the particle size is larger than 2−4 nm. Diameters of the studied dendrimers are in the 45−60 Å range,[30] thus these measurements suggest that the sizes of the metallic domains in the dendrimer nanocomposites may be much smaller than the size of the dendrimer.

We believe that there are fundamental differences in the morphology of the "classic" metal clusters[18,31] (which are composed of microcrystalline metals or materials surrounded by stabilizers)[32] and the metal containing dendrimer nanocomposites. At present, very little is known about the physics and/or chemistry of these fascinating materials.[33] Further experimental work is in progress to further clarify the structures of these nanomaterials both in our Laboratory as well as with other collaborating groups.

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Supporting Information Available: Details of the experimental procedures and characterization data (8 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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