Preparation of Cu Nanoclusters within Dendrimer Templates

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Here we introduce a new template-synthesis strategy for preparing metal nanoclusters within dendrimer “nanoreactors”. Proof of concept is demonstrated by preparation of Cu clusters but the approach will be applicable to any transition metal ions that can be extracted into the interior of a dendrimer and subsequently reduced. Clusters ranging in size from 4 to 64 atoms are prepared by partitioning of Cu^{2+} into the interior of a poly(amidoamine) (PAMAM) Starburst dendrimer and subsequent chemical reduction. By controlling the chemical structure and size of the dendrimers, different-size clusters can be prepared.

Small clusters of metals[1] and semiconductors[2] are interesting because of their unique mechanical, electronic, optical, magnetic, and chemical properties. Of particular interest are transition-metal nanoclusters, which are useful for applications in catalysis and electrocatalysis.[3−7] The per-atom catalytic efficiency of metal clusters and colloids often increases as the cluster size decreases. Unfortunately, as a consequence of the presence of many unsatisfied metal bonds, the probability of cluster aggregation also increases with decreasing size. The extent of agglomeration can be effectively reduced by lowering the surface energy by adsorption of stabilizers such as polymers or surfactants. However, in effect this corresponds to poisoning the cluster surface,[8−11] thereby marginalizing applications such as catalysis. A significant challenge, therefore, is the development of methods for eliminating aggregation without reducing catalytic efficiency. Another key challenge involves controlling cluster size and size distribution. There are two methods in common use for achieving this goal: (1) optimization of the synthesis conditions for cluster nucleation, growth, and growth termination and (2) growth of particles within monodisperse templates such as reversed micelles or porous membranes.[12−16] By using dendrimers as monodisperse templates for cluster growth, we achieve both cluster stability and full control over size and size distribution, while simultaneously allowing access of substrates to the cluster surface.[17,18]

Figure 1a shows absorption spectra of Cu^{2+} coordinated to different ligands. In the absence of dendrimer, Cu^{2+} exists primarily as $[Cu(H_2O)_6]^{2+}$, which results in a broad, weak absorption band centered at 810 nm. This corresponds to the well-known d−d transition for Cu^{2+} in a tetragonally distorted octahedral or square-planar ligand field.[19,20] In the presence of hydroxyl-terminated, fourth-generation (G4) PAMAM dendrimers having an ethylenediamine core (G4-OH), λ_{max} for the d−d transition shifts to 605 nm ($\epsilon \sim 100$ M^{-1} cm^{-1}, based on the equivalents of Cu^{2+} present). In addition, a strong band centered at 300 nm ($\epsilon \sim 4000$ M^{-1} cm^{-1}) emerges, which can be assigned to the ligand-to-metal-charge-transfer (LMCT) transition.[21−23]

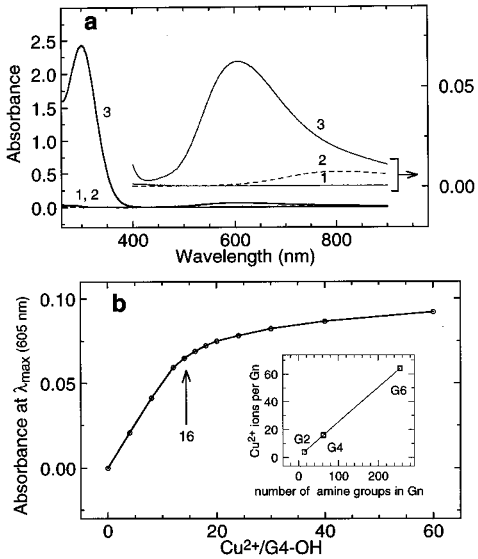

Figure 1. (a) Absorption spectra of 0.6 mM $CuSO_4$ in the presence (solid line, curve 3) and in the absence (dashed line, curve 2) of 0.05 mM G4-OH. Curve 1 is the absorption spectrum of 0.05 mM G4-OH vs water. (b) Spectrophotometric titration plot: absorbance at the peak maximum of 605 nm as a function of the number of Cu^{2+} ions per G4-OH. The initial concentration of G4-OH was 0.05 mM. The inset shows the relationship between the number of Cu^{2+} ions complexed within Gn-OH and the number of 3° amine groups within Gn-OH. The titration end point is estimated as the extrapolated intersection of the two linear regions of the curve before and after the equivalence point. The optical path length was 1 cm, the temperature was 20 ± 2 °C, and unbuffered aqueous $CuSO_4$ (pH ∼5.1) was used to titrate the unbuffered aqueous dendrimer solution (pH ∼8.1 for Gn-OH and pH ∼9.0 for G4-NH_2).

To learn more about the Cu^{2+} ligand field, we quantitatively assessed the number of Cu^{2+} ions extracted into each dendrimer by spectrophotometric titration (Figure 1b). The data indicate that each G4-OH dendrimer sorbs 16 Cu^{2+} ions. It is tempting to conclude that each Cu^{2+} ion is coordinated with about 4 amine groups since a G4-OH dendrimer contains 62 interior tertiary amines. However, we think it more likely that most of the ions bind to the outermost 16 pairs of tertiary amine groups because CPK models indicate that the dendrimer structure is not well configured for complexation between the inner most amines and Cu^{2+}. Thus, on average, each Cu^{2+} is coordinated to two amine groups, and the remaining positions of the ligand field are likely occupied by weakly binding ligands such as amide groups or water molecules.[24,25] This model is fully consistent with the results of spectrophotometric titrations of G2-OH and G6-OH, which contain 4 and 64 pairs of tertiary amines in the outermost shell,

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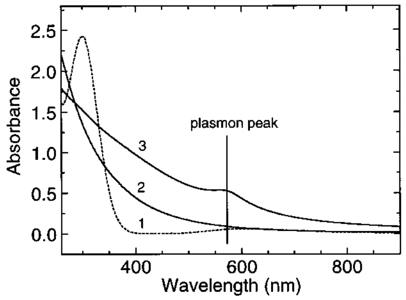

Figure 2. Absorption spectra of a solution containing 0.6 mM $CuSO_4$ and 0.05 mM G4-OH before (dashed line, curve 1) and after (solid line, curve 2) reduction with a 5-fold molar excess of $NaBH_4$. Curve 3 was obtained under the same conditions as those for curve 2 except 0.05 mM G4-NH_2 was used in place of G4-OH.

and which sorb 4 and 64 Cu^{2+} ions, respectively (Figure 1b inset). In addition, the EPR spectrum of Cu^{2+} coordinated within G4-OH yields a $g_{||}$ factor of 2.22 and a hyperfine coupling constant, $A_{||}$, of 189 cm^{-1} (see Supporting Information). These values are consistent with the presence of Cu^{2+} in a tetragonal ligand field consisting of 2 amines and 2 other nitrogen- or oxygen-containing ligands.[25−28]

The binding between Cu^{2+} and dendrimer is pH dependent. Depending upon the solution conditions, however, the sorption of Cu^{2+} within the dendrimer is irreversible: the d−d transition band at 605 nm does not decrease significantly even after 36 h of dialysis against pure water. However, H^+ effectively competes with Cu^{2+} for the tertiary amine sites,[29] and so it is possible to release Cu^{2+} from the G4-OH interior in a pH 1.3 HCl solution.

Chemical reduction of Cu^{2+}-loaded G4-OH dendrimers (G4-OH/Cu^{2+}) with a 5-fold molar excess of $NaBH_4$ results in intradendrimer Cu clusters. Evidence for this comes from the immediate change in solution color from blue to golden brown: the absorbance bands originally present at 605 and 300 nm disappear and are replaced with a monotonically increasing spectrum of nearly exponential slope toward shorter wavelengths (Figure 2). This behavior results from the appearance of a new interband transition arising from the formation of intradendrimer Cu clusters. The measured onset of this transitions at 590 nm agrees with the accepted value,[30] and the exponential shape is characteristic of a band-like electronic structure, which strongly suggests that the reduced Cu does not exist as isolated atoms, but rather as clusters.[31] This view is also supported by loss of signal in the EPR spectrum following reduction.[32]

The absence of an absorption peak arising from Mie plasmon resonance (around 570 nm)[33] indicates that the Cu cluster is smaller than the Mie-onset particle diameter of about 5 nm.[33,34] The plasmon resonance cannot be detected for very small metal clusters because the peak is flattened due to the large imaginary dielectric constant for small metal clusters.[31]

Transmission electron microscopy (TEM) results also indicate the presence of intradendrimer Cu clusters after reduction. Micrographs of Cu clusters within G4-OH reveal particles having a diameter less than 1.8 nm,[35] much smaller than the 4.5 nm diameter of G4-OH.[36,37]

Finally, the intradendrimer Cu clusters are extremely stable despite their small size, which provides additional strong evidence that the clusters reside in the dendrimer interior. Clusters formed in the presence of G4-OH or G6-OH dendrimers and with a Cu^{2+} loading less than the maximum threshold values (Figure 1b) were found to be stable (no observable agglomeration or precipitation) for at least 1 week in an oxygen-free solution. However, in air-saturated solutions the clusters revert to intradendrimer Cu^{2+} ions overnight. In contrast, when excess Cu^{2+} is added to a dendrimer solution, Cu^{2+} is present both inside the dendrimer and as hydrated ions in solution. After reduction, the excess Cu^{2+} forms a dark precipitate within a few hours, but the remaining transparent solution yields the same absorption spectrum as one prepared with a stoichiometric amount of dendrimer and Cu^{2+}. TEM images of the particles in these solutions reveal two size regimes: the first is 9 ± 4 nm in average diameter and is responsible for the dark precipitate; the second, which is estimated to have an upper limit of 1.8 nm in diameter,[35] corresponds to the intradendrimer cluster.

The ability to prepare well-defined intradendrimer metal nanoclusters depends strongly on the chemical composition of the dendrimer. Spectroscopic results such as those shown in Figure 1 indicate that when amine-terminated G4 PAMAM dendrimers (G4-NH_2) are used as templates, they sorb a maximum of 36 Cu^{2+} ions which bind primarily to the terminal primary amine groups. Reduction of a solution containing 0.6 mM $CuSO_4$ and 0.05 mM G4-NH_2 results in a clearly observable plasmon resonance band at 570 nm (Figure 2),[31,33,34] which indicates that the Cu clusters prepared in this way are >5 nm in diameter. This larger size is a consequence of agglomeration of Cu particles adsorbed to the unprotected dendrimer exterior.[29,38]

In conclusion, using dendrimers as a synthetic template and as a cluster stabilizer, we have developed a new method for preparing stable metal nanoclusters composed of a well-defined number of atoms. Importantly, cluster size can be controlled by varying the size of the host-dendrimer nanoreactor. At present we believe that some fraction of the cluster surface is not coordinated to internal dendrimer branches, which may make these materials uniquely suited for catalysis. Experiments are underway to test this idea and better characterize these fascinating new nanocomposite materials.

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Note Added in Proof. We have recently become aware that results similar to those reported here have been obtained by Tomalia et al. (Michigan Molecular Institute, Midland, MI).

Supporting Information Available: Absorption spectra of solutions of 3.0 mM Cu^{2+} and 0.05 mM Gn-OH ($n = 2$, 4, and 6) and spectrophotometric titration plots of G4-NH_2 and G4-OH with Cu^{2+}; pH effect on the absorbance of solutions of 0.6 mM Cu^{2+} and 0.05 mM G4-OH, and 1.5 mM Cu^{2+} and 0.05 mM G4-NH_2; EPR spectra ($T = 140$ K) of solutions of 0.6 mM Cu^{2+} and 0.05 mM G4-OH before and after reduction (3 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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