**The Mechanism of Photoreduction of Copper Ions Complexed to Amine-Terminated Functionalities**

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**Motivation**

Dendrimers are highly branched, three-dimensional globular macromolecules that have distinct characteristics and properties. The chemical functionalities of poly(amidoamine) (PAMAM) or poly(propyleneimine) (PPI) dendrimers provide sites for metal cation coordination. Subsequent chemical reduction, usually with sodium borohydride, produces metallic-dendrimer nanocomposites. An alternative method for reducing metal ions has become known through employing UV photoreduction to the metal ion-dendrimer complex without the need of additional reactants. Researchers stated the idea of photodecomposition of the dendrimer that yields carbonyl compounds that may induce reduction.

In this study, we focus our attention on determining the source of electrons within the dendrimers that are used to reduce the metal ions during photoreduction.

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**Probe Molecules for Investigating Photoreduction Mechanism**

Several molecules with amine functionalities were used to investigate the mechanism of the photoreduction process. However, only the 1-hydroxyurea molecule complexed with Cu²⁺ ions. TEM images revealed the metal-hydroxyurea complex did not produce any nanoparticles after irradiation with UV light.

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**Photochemical Reduction**

EPR spectra (above) of a) Cu²⁺ with G0 dendrimer before irradiation and b) Cu²⁺ with G0 dendrimer after 45 min irradiation in toluene at 77 K. Irradiation was conducted with a mercury lamp (λ_{max} = 254 nm).

UV-vis spectra (right) of Cu²⁺ complexed with PAMAM and PPI dendrimers. Reduction of Cu²⁺ is evident (PAMAM solution) with increasing slope, which strongly suggests aggregation among Cu atoms. Reduction of Cu²⁺ is not evident (PPI solution) since the before and after irradiation appears similar.

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**Conclusions**

Results have shown that there are crucial criteria in the photoreduction process: (1) coordination and the number of amine sites are critical for particle formation; (2) tertiary and secondary amines contribute major roles in providing electrons for reducing Cu²⁺ from nitrogen radicals.

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