**Sudhanshu Srivastava: Research Summary 2006**

My research in Prof. Rotello group is focused on wide range of topics, from organic synthesis to fabrication of novel nano-materials. The underlying theme common through these projects, however, has been the study of self-assembly. In particular, my work has focused on self-assembly of nanoparticles, both gold and iron oxide with dendrimers, polymers and proteins. Our aim was to first understand the driving forces governing the assembly process, and then apply this insight to control the structure of the resulting material and tailor its function.

**I) Nanoparticles for Materials Applications:**

Nanoparticles provide versatile tools for materials applications as they feature unique electronic, magnetic and optical properties associated with their core material. Self-assembly of nanoparticles present an excellent tool to bridge the gap between the synthetic "bottom up" and lithographic "top down" assembly approaches.

***a) Nanoparticle Assembly with Dendrimers (Polymers)***

The present study utilizes the 'bricks and mortar' method, where dendrimer (polymers) were used as mortar' and nanoparticles as 'bricks'. Non-covalent assembly mechanisms were used in exploring nanocomposite structures such as morphology, interparticle distance, and achieving materials with tunable properties. The nanoparticles were synthesized and assembled with a series of PAMAM dendrimer generations ($G_0$, $G_1$, $G_2$ and $G_4$) providing a systematic increase in interparticle spacing. In this approach, dendrimers were used as spacers, (a) to control the optical behavior (Surface Plasmon Resonance (SPR)) (Figure 1) and (b) modulation of magnetic properties (Blocking Temperature) based upon the nanoparticles (gold and iron oxide) dipole-dipole interactions. Nanoarticles with lower dendrimer generation showed larger dipolar interaction in comparison to bigger dendrimer generations. Gold nanoparticles were studied for the modulation in SPR based upon the change in dipolar interactions. Similarly, super-paramagnetic iron-oxide nanoparticles were studied for tuning of blocking temperatures with an increase in dipolar coupling. Dendrimers display sequential spacers for controlled structures and tuning the collective response (optical and magnetic) of the material. The collective response of the nanocomposite with tunable properties based upon dipolar coupling of nanoparticles paves the way for the creation of novel functional materials.

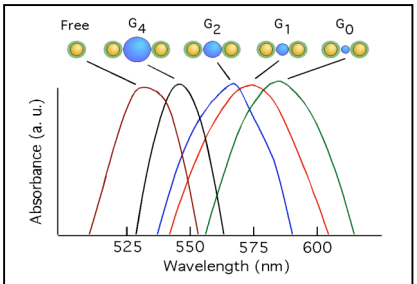


**Figure 1.** Schematic presentation of SPR for nanoparticles assembled with different PAMAM generations.

***b) Nanoparticle Self-Assembly: Proteins as building blocks***

To create nanocomposites with higher spacings and to include the additional functional property of the spacers, the use of proteins as building blocks was explored. Most of the protein-nanoparticle assemblies are limited to the utilization of specific interactions between biotin and streptavidin or an antigen and an antibody to generate nanoparticle aggregates. However, such approaches provide limited control over nanoparticle ordering. As an alternate approach, we sought to use the inherent properties of proteins to direct the self-assembly of nanoparticles into controlled composites. The advantages are (a) the nanocomposites with well-defined interparticle spacings, can be obtained and (b) this provides a facile route to incorporate protein function into the nanoparticle ensembles, thereby greatly expanding the scope for development of new functional materials.

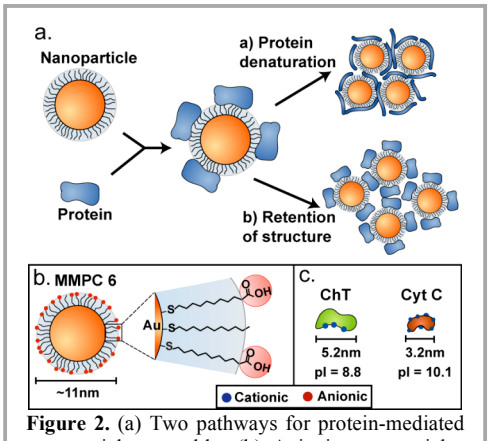


**Figure 2.** (a) Two pathways for protein-mediated nanoparticle assembly. (b) Anionic nanoparticles assembled with (c) two cationic proteins, chymotrypsin (ChT) and cytochrome c (Cyt C).

As an initial step towards this direction, we envisaged two pathways for protein-mediated nanoparticle assembly: (a) protein denaturation on the nanoparticle surface, providing a closed packed assembly and (b) retention of native protein structure and volume, enabling nanoparticles to be spaced by larger interparticle spacings (Figure 2). This approach was probed using two proteins, chymotrypsin (ChT) and cytochrome c (Cyt C) for assembling the nanoparticles. The two proteins are similar in size and overall surface charge, however, vastly different in structural stability. This approach provides a novel way to utilize the inherent structural stability of proteins for obtaining nanoparticle ensembles with controlled interparticle spacings.

A similar study was followed by exploiting the unique surface adsorption properties of lysozyme, an ellipsoidal, highly charged and robust protein, for directing the self-assembly of gold nanoparticles into composites featuring tunable interparticle spacings and modular collective optical responses.