

## An Alternative Motif for the Controlled and Reversible Self-assembly of Nanoparticles, a proposal to the Center for Nanohybrid Functional Materials (CNFM) for exploratory investigation.

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The proposed project is relevant to *Nanohybrid Fabrication*, the preparation of highly ordered spatially coherent 3-D nanostructures and their hybridization with chemical or biological sensing elements, and *Molecular Interactions within Nanohybrid-based devices*, exploiting potential sensing applications based on molecular interactions within nanohybrid-based devices.

Directed self-assembly<sup>1</sup> of nanoparticles into specific structures can provide controlled fabrication of nanometer-sized building blocks with unique and potentially useful electronic, optical, magnetic and catalytic properties.<sup>2</sup> This capability will be of particular importance in applications where the parallel self-assembly of a number of different nanoscale building blocks onto a common substrate is to be exploited. The most frequent approach toward this goal, oligonucleotide-directed self-assembly, is currently unmatched in its exquisite selectivity and near unlimited sequence programmability. For example, Figure 1 shows the self-assembled pattern of silver nanoparticles around gold nanoparticles.<sup>3</sup>

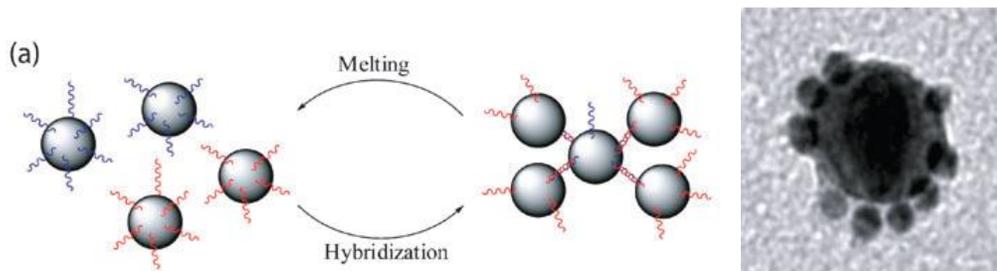
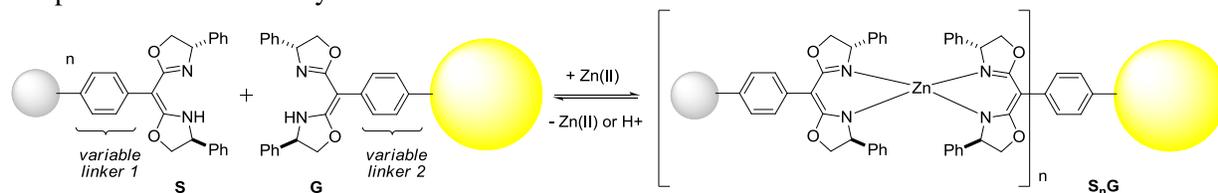


Figure 1. Nucleotide directed self-assembly of silver nanoparticles around gold nanoparticle

The oligonucleotide approach, however, does have some significant drawbacks. While oligonucleotide-directed self-assembly offers near unlimited sequence programmability, there are at present no applications that exploit the encoding for more than binary combinations of nanometer-sized building blocks. While the hybridization between complementary strands, and hence self-assembly, is facile, the reverse (i.e., melting) is more challenging since rehybridization is facile. This can limit applications directed toward environmentally responsive self-assembly and sensing. In addition, the chemistry required for specifically labeling oligonucleotides to enable their attachment to the nanoparticle remains synthetically challenging and of limited scalability. Once fabricated, such systems are inherently labile toward nucleases, which are omnipresent in the environment. For these reasons and others, it remains desirable to devise alternative methods to direct nanoparticle self-assembly.

We have pioneered the use of chirality directed self-assembly of bisoxazoline (box) complexes for the synthesis of functional materials, specifically, novel donor-acceptor complexes<sup>4</sup> and supramolecular catalysts.<sup>5</sup> In this present proposal we aim to carry out proof-of-principle experiments to demonstrate the use of programmable metal-directed self-assembly for fabricating complex self-assembled patterns of nanoparticles and make samples available to others in the CNFM to develop collaborative studies. While space does not permit a detailed discussion of the chemistry proposed in Scheme 1, it follows from our previously published results. Box-functionalized silver nanoparticles (**S**, grey spheres) will be combined with a complementarily box-functionalized gold nanoparticle (**G**, yellow spheres) to give the nanoparticle assemblies  $S_nG$  (where  $n$  = the number of silver nanoparticles). Among the advantages offered by this approach are the ability to introduce a variety of functional groups, electronic characteristics (i.e., insulating or conducting) and display profiles via the choice of the linkers. For example, the box derivative and variable linker can be modified so that the functional group point of attachment to the

nanoparticles can be SH, NH<sub>2</sub>, COOH, PO(OH)<sub>2</sub> or PPh<sub>2</sub>. This is important to enable the assembly of two different types of nanoparticles. For example, one linker may contain a thiol terminus while the other has a carboxylic acid. This enables selectively bonding to a gold nanoparticle via the thiol and to a titanium nanoparticle via the carboxylic acid.



Scheme 1. A proposed macromolecular ligand to be utilized in the proposal

Self-assembly will be characterized using standard microscopic and spectroscopic methods. As seen in Figure 1, microscopic methods will give direct visualization of self-assembly and its pattern. Changes in plasmon resonance as well as Soret bands will give an idea about nanoparticle connectivity. In some cases it may be possible to detect self-assembly process by naked eye due to color changes of the solution.

By judicious choice of the variable linkers, it is expected that it will be possible to control the length scale of the self-assembled band, that is, program the distance between nanoparticles. Self assembly can be controlled in two dimensions using branched or dendritic linkers; this also opens the possibility of precisely controlling the number of nanoparticles in  $S_nG$  and related systems, a feature that, to date, has only demonstrated for oligonucleotide systems. By tuning the linkers it should be possible to make self-assembly patterns in various forms including, for example, super-lattices, satellite nanoparticles, nanoflowers, single or multiple nanotriangles having one nanoparticle as the common corner etc.<sup>2</sup> Conjugated linkers can be used to make a molecular wire like connection between different nanoparticles. Self-assembly is readily reversed by changing the pH or by the addition of certain ions and small organics that affect the co-ordinate bonds between nitrogen atoms and Zn. Thus, it is expected that  $S_nG$  or related systems can be used in sensing, for example, by designing fluorescence quenching or generation upon self-assembly for the detection of the species that promote or reverse self-assembly.

In summary, this application seeks seed funds to carry of proof-of-principle studies directed toward a new motif for the programmed self-assembly of nanoparticles. Funds will be used to extend the appointment of a current postdoctoral with experience in both organic and nanoparticle synthesis and provide some funds for supplies and facilities use. The specific aim is to produce  $S_nG$  and related systems in sufficient quantity for characterization and preliminary applications as sensors. It is hoped that the availability of  $S_nG$  and related systems will stimulate collaborations with other CNFM members.

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- <sup>4</sup> Atkins, J. M.; Moteki, S. A.; DiMagno, S. G.; Takacs, J. M. "Single Enantiomer, Chiral Donor-Acceptor Metal Complexes from Bisoxazoline Pseudoracemates" *Org. Lett.* **2006**, *8*, 2759-2762 (DOI:10.1021/ol060836s).
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