

## CHARACTERIZATION OF THE MOLECULAR CHEMISTRY OF METAL-BASED NANOBEADS ON A GOLD SURFACE

Jayna Chan, Martin J. Stillman, Peter R. Norton

University of Western Ontario, London, Ontario, N6A 5B7 CANADA

E-mail: [jchan3@uwo.ca](mailto:jchan3@uwo.ca)

The research described in this paper explores the changes in structural and electro-optic properties of designer metal-based nanobeads located in close proximity to a gold surface, exploiting techniques in molecular biology, molecular modeling, and scanning tunneling microscopy.

Nature has provided us with metalloproteins that form nanobeads (Fig. 1a, 1b) that comprise metal-thiolate clusters, which are analogues of CdS, CuS, ZnS, and AgS nanoparticles, tightly wrapped within a peptide strand. Using recombinant techniques, we have designed and synthesized novel chains of nanobeads of variable length (in collaboration with Dr. P. Kille, University of Cardiff, Wales) with high yield and purity.[1] This affords us the ability to pattern the nanobeads on the gold surface. The nanobead properties can be tuned by metal ion exchange to form clusters of Cd-S, Cu-S, Zn-S, or Ag-S (Fig. 2) in which different electronic properties (redox, spectroscopic) arise from both the metal itself and coordination geometry (2, 3, or 4-fold).

We use molecular modeling to investigate the changes in molecular chemistry and structure of these metal-cluster nanobeads and their interactions with a gold surface.[2] Calculations based on MM3/MD techniques (CACHe v6.1, Fujitsu America) provided energy-minimized models that are good approximations of predicted structures of the nanobeads. Additional metal-thiolate interactions have been incorporated into an existing MM3 force field to account for the coordination of the metals.

We have developed a novel method of calibrating the MM/MD models using XANES spectroscopy. XANES spectroscopy is a method that is highly sensitive to coordination geometries and bond lengths. In this method, we calculate metal XANES spectra from atomic coordinates taken from MM3/MD simulations, and compare them to experimental XANES spectra.[3]

Molecular dynamics simulations currently carried out on the interaction of a double nanobead structure with a gold 111 surface, indicate two interesting phenomena (Fig. 3). Firstly, the exposed cysteinyl sulfurs are in close proximity to the gold surface, suggesting weak average Au-S bond formation is possible between the nanobead and the surface, and secondly, adjacent domains are orthogonal to each other. From this we hypothesize that one crevice may act to anchor the protein to the surface, and the other available for chemistry, which would allow *in situ* modifications.[4,5]

Finally, Scanning Tunneling Microscopy (STM) is used to probe the electronic structure of the nanobeads on a conducting gold surface, generating surface images that can be used to obtain molecular structure and orientation information.

## References:

- [1] Z. Huang, J. Chan, and M. J. Stillman (2004) (Manuscript completed; to be submitted in May to Proteins).
- [2] J. Chan, Z. Huang, M. E. Merrifield, M. T. Salgado, and M. J. Stillman, *Coordination Chemistry Reviews*, **233-234** (2002) 319.
- [3] J. Chan, M. E. Merrifield, A. V. Soldatov, and M. J. Stillman (2004) (Manuscript under revision; to be resubmitted in May to Inorg. Chem.).
- [4] Armstrong *et al.*, *Faraday Discuss*, **116** (2000) 191.
- [5] K. Chattopadhyay, S. Mazumdar, *Bioelectrochemistry*, **53**(1) (2001), 17.

## Figures:

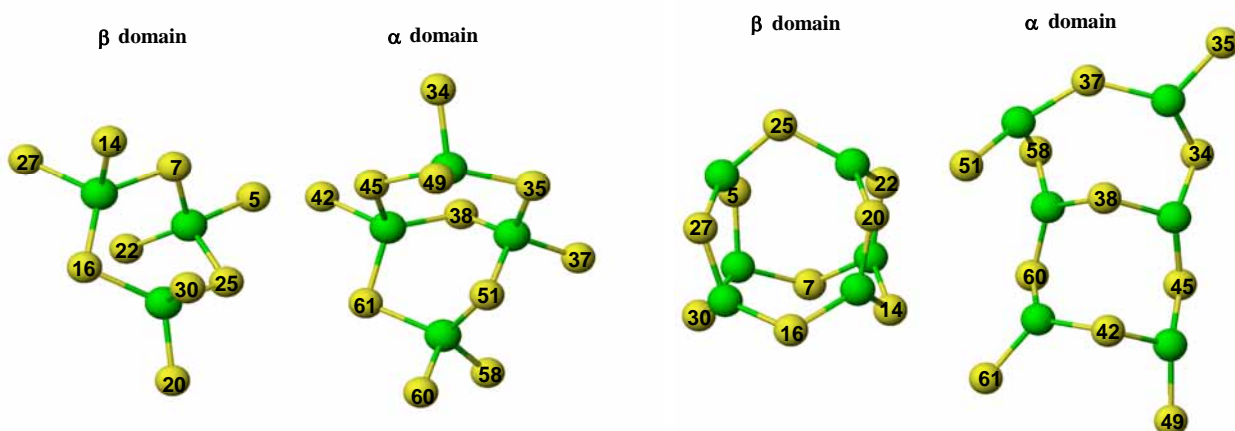


Fig. 1a. Metal-thiolate clusters of two different nanobead configurations coordinated by tetrahedral cadmium where the green spheres represent divalent cadmium cations and the yellow spheres represent sulfur groups.

Fig. 1b. Metal-thiolate clusters of two different nanobead configurations coordinated by digonal and trigonal copper where the green spheres represent monovalent copper cations and the yellow spheres represent sulfur groups.

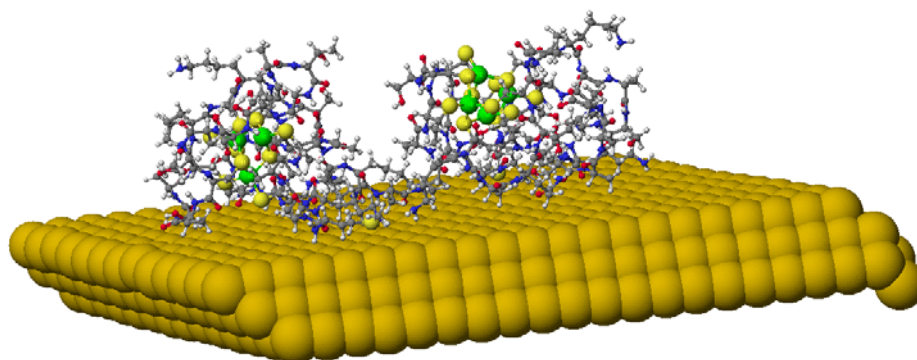


Figure 3. Energy minimized structure of a double nanobead structure interacting with a Au(III) surface through an exposed sulphur the nanobead shown at the left. Minimization was carried out by a combination of molecular mechanics and molecular dynamics.