

Lectins are sugar-binding proteins or glycoproteins that recognize specific carbohydrate structures and agglutinate various types of animal cells. In marine animals, lectins are believed to contribute as non-self recognition factors to the defense mechanism. Interestingly, it has been theorized that some lectins from marine animals mediate the interaction between symbiont and host. SLL-2 is a D-galactose binding lectin isolated from an octocoral, *Sinularia lochmodes*. It was found that SLL-2 was distributed densely on the surface of symbiotic dinoflagellate *Symbiodinium* sp. cells. Previous report showed that SLL-2 transforms free-swimming stage *Symbiodinium* cells into non-motile stage *Symbiodinium* cells and keep them in their non-motile stage [1,2]. These results show that SLL-2 is a chemical cue in the symbiosis between dinoflagellates and coral. The three-dimensional structure of SLL-2 will provide information about the symbiosis mechanism.

The structure of SLL-2 was determined by the molecular replacement method using atomic coordinates of *Helix pomatia* agglutinin (HPA lectin, PDB code: 2ccv) as a search model. Three SLL-2 monomers form a trimer around a non-crystallographic 3-fold axis, and two trimers form a hexameric assembly using hydrogen bonds of three pairs of elongated strands from each monomer. The crystal structure of SLL-2 monomer shows the beta-sandwich lectin fold with six strands. The sites of N-glycosylation and sugar binding ("site 1") were identified clearly in the monomer structure. In the hexameric molecule, two of the six "site 1"s possess galactopyranoside derivative that might come from the N-glycosylation site, three contain the precipitant molecule, and the remaining one accommodate a water molecule. Crystals from low monosaccharide (GalNAc: N-acetyl-D-Galactosamine) concentration holds three GalNAcs and three precipitant molecules in its "site 1"s. The crystal structure of SLL-2-GalNAc complex from sugar-rich environment indicated that GalNAc molecules bind to all "site 1"s. These observations reveal that SLL-2 can maintain both unsymmetrical and symmetrical hexameric molecule stably across various environments. In addition, a large electron density, which appears for a part of oligosaccharides but was not enough to ensure the bound species and its orientation, was observed at extra sugar binding site, "site 2". From these results, we could propose binding mode of the pentasaccharide, which is the unbranched polysaccharide recognized by HPA lectin, to SLL-2, and the function of the SLL-2 in the symbiosis between dinoflagellates and coral.

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### Interface Plasmon in Pseudo One-dimensional Si/SiO<sub>2</sub> core-shell Nanostructures by Electron Energy Loss Spectroscopy

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Surface/interface plasmons (IP) in nanostructured materials has generated much interest for their potential applications in plasmonic devices, in particular, those can be operated beyond the diffraction limit of light. While the plasmonic properties of nanomaterials are commonly studied using optical approaches, the best spatial resolution achieved is a fraction of optical wavelength, i.e., ~50 nm. Consequently, mapping of plasmonic properties at higher spatial resolution and imaging of nanostructures of smaller than about 50 nm remains

difficult. On the other hand, TEM-EELS has been recently employed as alternative technique for such purposes [1]. The excellent spatial resolution of the technique enables the mapping of local variations in the material's dielectric response at nanometer scale. Although caution has to be taken, qualitative agreement between the EELS results and material's photonic response make it a powerful tool in probing the local plasmonic properties of nano-objects. Furthermore, the TEM allows to obtain chemical and structural information from the *same* area as the plasmon maps.

The interface plasmon in pseudo one-dimensional Si/SiO<sub>2</sub> core-shell nanostructures have been investigated using electron energy loss spectroscopy (EELS)-related techniques under parallel illuminations, which results are comparable to those obtained by optical methods.

Elongation from a perfect spheroid Si/SiO<sub>2</sub> core-shell nanoparticle to nanorod, and eventually to a long nanowire, results in splitting of the IP modes to a transverse and a longitudinal branch. The longitudinal IP mode red shifts with the aspect ratio increase of the nanoparticle, due to the larger charge separation distance along the long axis of the nanostructure. Retardation effect comes into play in longer nanostructures, leading to periodical pile up of opposite charges. This is revealed by the uniform intensity along the longitudinal direction of the long Si/SiO<sub>2</sub> nanocable in the energy filtered image. The small diameter of the nanostructure determines the dominance of the longitudinal mode in the IP oscillation. Consequently, the optical absorption of small-diameter nanostructures is significantly different from that of the larger ones.

Assembly of the Si nanoparticles into one-dimensional particle chains leads to interaction between the adjacent nanoparticles, which can also induce the splitting of the interface plasmon into transverse and longitudinal polarizations. In addition, such coupling causes spatial re-distribution of the IP intensity, leading to local field enhancement in-between the two nanoparticles. By controlling the growth of Si nanostructures into different morphologies, we demonstrate that the material's optical properties can be manipulated.

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### Radiation damage and electron energy loss spectroscopy of Au particles on amorphous Ge substrates

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Ideally the morphology, structure, and electronic properties from an individual nanoparticle would be obtained in a (scanning) transmission electron microscope (S)TEM experiment at an irradiation dose that does not lead to appreciable sample damage. Gold nanoparticles are of interest as catalysts and as building blocks of plasmonics devices. Irradiation of Au particles by an electron beam results in both hopping of individual Au atoms, observed in extremely small clusters, and in frequent change of orientation of particle with respect to the incident electron beam, observed even in particles with volume more than (10)<sup>3</sup> nm<sup>3</sup> [1].

A TEM/STEM equipped with a cold field electron source and an electron energy loss (EEL) spectrometer can be used to obtain all the

above information. We used nano beam diffraction to obtain particle structure and orientation at low irradiation dose and spatially resolved valence electron energy loss spectroscopy to measure the optical properties of the same nanoparticles. The use of spatially resolved EELS together with approximately 0.35 eV energy resolution of our instrument allows us study spatial origin of the spectral features. Component deconvolution can be used on spatially resolved EELS spectra to separate the Au particle contribution to EEL spectra from the substrate contribution [2].

To optimize our Hitachi HF 3300 microscope and evaluate its suitability we used a sample of gold nanoparticles deposited onto an amorphous germanium substrate. We used 100 kV incident energy and collected 50 spatially resolved spectra with 5 s acquisition time. We then acquired nano beam diffraction patterns and energy filtered series to measure local sample thickness.

It appears that the even very small Au particles are composed of several crystallites. The spatially resolved EELS reveals strong peaks at about 2.25 eV and at about 5.5 eV corresponding to surface and bulk plasmon for a particle of approximately spherical shape [3]. We also find that although the overall shape of the Au particles appear to be largely intact after about 50 C/cm<sup>2</sup> at 100 kV, the 3 nm to 5 nm thick amorphous germanium is entirely removed at the same dose. The electron sputtering threshold for Ge is about 115 keV, taking Ge atom desorption energy  $E_D$  to be equal to sublimation energy  $E_S$ , or 181 keV if  $E_D = (5/3)E_S$  [4]. The microscope vacuum is  $3 \times 10^{-8}$  torr during our experiments excluding chemically enhanced etch by gaseous species from microscope vacuum. Therefore sputtering is unlikely to explain the fast damage of the amorphous Ge film. The amorphous Ge film appears to be protected in the areas where Au particles are located.

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### Molecular Spin Crossover – What can pressure reveal?

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The spin crossover (SCO) phenomenon is the switching of a transition metal complex between its high spin (HS) and low spin (LS) electronic configurations as a result of some perturbation to the species (e.g. changes in temperature or pressure, or after light irradiation). Molecular species in the HS and LS states are distinguished by differences in their structure, color and magnetic moment [1].

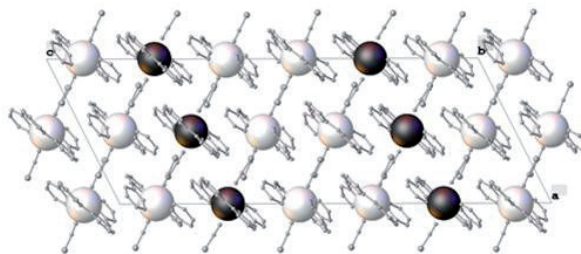
In this class of materials the local and long-range structure directly impacts the magnetic behavior of the sample in a dramatic way. Understanding this relationship is crucial to the development of applications that exploit these switchable properties in the fields of molecular electronics, data storage and sensing.

High pressure studies may permit the decoupling of structural and spin-state transitions and thus allow access to unique phases that cannot be investigated using more conventional diffraction methods alone.

Single crystal X-ray diffraction techniques at elevated pressure and variable temperatures, complimented by high pressure Raman spectroscopic and magnetic studies, have been used to probe the structure-properties relationship of the molecular materials [Fe(babppy)(NCS)<sub>2</sub>] [2] and [{Fe(bpp)(NCS)<sub>2</sub>}<sub>2</sub>·4,4'-bipy]MeOH [3]. The former undergoes an unprecedented pressure-induced two-step

SCO; it is characterized by an ordered intermediate phase with long range order of [HS-LS-LS] sites within the lattice in the pressure range 4-11 kbar (see image). The latter material undergoes a gradual spin conversion under pressure, which is in stark contrast to its rather abrupt thermal SCO behavior.

These examples serve to illustrate the wealth of information, obtained through high pressure studies of functional molecular materials, which is often vital to understanding complex ambient pressure behavior.



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### Reversible structural modulation and magnetic properties in a Co-based SMM

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The topological properties of transition metal citrate cubanes lead to a variety of structure types and topotactic reactivity in the crystalline state. The citrate cubane, with general formula [M(II)<sub>4</sub>(citr)<sub>4</sub>]<sup>(8-)</sup> [M = transition metal, citr = quadruply deprotonated citrate, C<sub>6</sub>H<sub>4</sub>O<sub>7</sub><sup>(4-)</sup>], has been prepared with two distinct topologies in Co(II) and Mn(II) complexes.

Within this context, a cubane-based Co(II) complex is described -- Co<sub>4</sub>(citr)<sub>4</sub>[Co(H<sub>2</sub>O)<sub>4</sub>]<sub>4</sub>, **2**, which was prepared in a two-stage process beginning with isolation of a sub-periodic crystalline material, **1**, whose modulated structure and chemical composition have been analyzed using single-crystal x-ray diffraction.

A reversible solid-state reaction can be provoked in **1** to yield **2**, whose three-dimensional structure is not modulated. The modulated structure of **1** is explained in terms of concerted hopping of peripheral Co(II) between neighboring molecules in **2**, producing a distinct chemical species.

Magnetic measurements conducted on the 1/2 single molecule magnet (SMM) system required special precautions to avoid interchange of the two species under experimental conditions. The distinct magnetic properties of the two interchangeable solids establish both as being based on SMM.

For **1** the average structure has  $a = 23.2064(14)$ ,  $b = 9.6655(4)$ ,  $c = 23.5066(11)$  Å,  $\beta = 111.037(6)^\circ$ ,  $V = 4921.2(2)$  Å<sup>3</sup>, space group *C2/c*. The refined modulation vector parameters are of the form  $(0\beta 0)$ , with  $\beta$  near 3/8. For the unmodulated structure of **2**,  $a = 22.7842(10)$ ,