

# Novel Organometallic Nano-structures with Fine-controlled Soft-landing for Designed Functional Surfaces

Atsushi Nakajima

Keio University & JST-CREST,  
Faculty of Science and Technology, Department of Chemistry,  
3-14-1 Hiyoshi, Kohoku-ku, Yokohama 223-8522, Japan  
E-mail: nakajima@chem.keio.ac.jp

Binary systems are very important to create functionality of materials, and binary clusters consisting of a few to hundreds atoms provide microscopic viewpoints toward chemical bonding, geometry, and electronic structures including spin states. For metal and organic ligands, a variety of 1D, 2D, and 3D structures are formed depending on their combinations, and they exhibit novel electronic properties, such as electron delocalization and multiple charge transfers [1]. My talk will be covered with (a) isolated binary and organometallic clusters and (b) soft-landed organometallic clusters.

## (a) Isolated binary and organometallic clusters

Metal-encapsulated silicon cage clusters are a new class of clusters and are opening up new avenues for silicon-based nanoscale materials. We present experimental evidence for a highly stable cluster corresponding to  $M@Si_{16}$  ( $M=3d$  transition metals). Mass spectrometry coupled with adsorption reactivity experiments and anion photoelectron spectroscopy show that the cluster features an electronically closed  $M@Si_{16}$  core as well as a metal encapsulated structure.

With the aid of proper organic ligands, furthermore, 1D structures are preferably formed in gas phase reaction. For example,  $Eu_m(COT)_n$  sandwich clusters were produced in gas phase by mixing the vapor of europium (Eu) atoms and 1, 3, 5, 7-cyclooctatetraene (COT) molecules and 18-layered clusters were produced at maximum, which is about 8 nm length. Formation mechanism and electronic structures will be presented in the viewpoint of electronic structures for  $Eu_m(COT)_n$ .

In the design of molecular magnetic materials, a subject to conquer is how to align the spin in the cluster. One-dimensional sandwich clusters are an interesting target since their magnetism should reflect geometric anisotropy and the condition of electronic spins on each layer. In this study, vanadium-benzene sandwich clusters were produced and the magnet deflection profiles of the cluster beam were measured (the Stern-Gerlach experiment). In the presence of inhomogeneous magnetic field, peaks for each sandwich clusters displayed the symmetric broadening and larger sandwich clusters show the successive increase of  $\mu_z$  up to  $n = 4$ . The plausible mechanism of ferromagnetic interaction is an intra-atomic exchange interaction within the d orbitals along with a partial charge transfer between the  $d_\delta$  and LUMO of benzene molecule.

## (b) Soft-landed organometallic clusters

We have successfully achieved non-destructive deposition of  $V_n(Bz)_{n+1}^+$  onto the self-assembled monolayer (SAM) surface. The Bz-ring breathing mode, which is the specific vibration of sandwich-structured clusters, was observed in the IR spectra at  $957\text{ cm}^{-1}$  for  $V(Bz)_2$  and  $956\text{ cm}^{-1}$  for  $V_2(Bz)_3$ . These results indicate that deposited clusters keep the sandwich-structure on the SAM coated Au(111) substrate. The peaks of the thermal desorption spectra appear at  $\sim 285\text{ K}$  for  $V(Bz)_2$  and at  $\sim 470\text{ K}$  for  $V_2(Bz)_3$ . This indicates that the thermal stability of  $V_2(Bz)_3$  is much higher than  $V(Bz)_2$ . By modification of the surface, the stability and the orientation of the clusters can be controlled to design the function of the cluster-decorated surface.

[1] A. Nakajima and K. Kaya, *J. Phys. Chem. A* **104**, 176-191 (2000).