

THE SUMMARY OF Ph.D. DISSERTATION

School of Integrated Design Engineering	Doctor Identification Number	MIYAJIMA, Ken
Title		
Electronic and Magnetic Properties of One-Dimensional Organometallic Clusters in Gas Phase		
Abstract		
<p>It is an important subject of research for material science to develop functional materials which possess novel optical, magnetic, and catalytic properties by structural regulation in atomic or molecular level. The fundamental unit which materializes functions is supposed to be nano-meter size which consists of tens to hundreds of atoms. Recently it has become clear that distinctive multi-component nano-clusters indeed can be produced by the application of the laser vaporization technique in gas phase.</p> <p>The aim of this work is the elucidation of the electronic and magnetic properties of the one-dimensional organometallic clusters which are produced by the application of the laser vaporization and molecular beam methods. The variety of the property of organometallic nano-cluster was demonstrated through the observation of electronic states, charge distributions, and spin states of the clusters by photoionization spectroscopy, chemical probe technique, and Stern-Gerlach type magnetic deflection experiment, respectively. The target of this work was focused on one-dimensional sandwich organometallic clusters of (a) vanadium, and (b) lanthanide(Ln) metals.</p> <p>(a) Vanadium-benzene organometallic clusters: In the V-benzene clusters, the d-π interaction plays an important role to form bondings. In this work, the quasi-band electronic structure due to the one-dimensional sandwich structure has been revealed successfully by the observation of the discrete ionization channels from the bonding dδ orbital in the photoionization efficiency measurement, which was actually in agreement with the calculated values by the simple Hückel method. On the other hand, the increase of the magnetic moment with the size was found, and the result evidently shows that each unpaired electron in non-bonding dσ orbital, which is localized on the metal atom, takes the ferromagnetic arrangement.</p> <p>(b) Lanthanide organometallic clusters: Ln-1,3,5,7-cyclooctatetraene (C₈H₈; COT) clusters are formed through ionic bondings. In the cluster, Ln atoms are stabilized by taking the charged states of Ln²⁺/Ln³⁺, and COT molecules become COT²⁻ which satisfies the aromaticity. In this work, one-dimensional Ln-COT (Ln = Eu/Ho) clusters were reacted toward Na/Cl atoms. The number of attached Na/Cl atoms can be reasonably explained by charge distributions of the ionic complex. From the measurement of the magnetic moment of Ln_nCOT_{n+1} (Ln = Pr, Eu, Tb, and Tm) clusters, the spin relaxation was observed. Magnetic moment of each cluster can be explained roughly by the magnetism of their free metal ions. It is an important viewpoint for materialize to create Ln containing organometallic clusters which is stable in the atmosphere. Thus ligands which possess strong complexation and bulkiness were introduced. By the introduction of the phthalocyanine (Pc), which is robust thermally, in the gas phase, the Ln_n(Pc)_{n+1} cluster was generated successfully. The electronic structure of Ln(Pc)₂ cluster was investigated by the photoionization spectroscopy and photoelectron spectroscopy.</p> <p>The electronic and magnetic properties of one-dimensional organometallic clusters were investigated by the application of the generation and spectroscopy technique as stated above, and their character was elucidated as a functional unit.</p>		