

RESEARCH ACTIVITIES V

Department of Applied Molecular Science

V-A Design of Spin-Functional Nanomaterials through Molecular Programming and Nanostructuring

Metal ions with d^4 – d^7 electron configurations can adopt two different magnetic states, *i.e.*, high-spin and low-spin states, which can cross over thermally or by electronic excitation. Spin-crossover phenomena have attracted attention in relation to their potential applications in molecular electronics. A fundamentally important challenge is to synthesize soft spin-crossover materials that can respond to external stimuli such as light and electric/magnetic fields. Up to date, inorganic and crystal engineering approaches have been employed for the synthesis of crystalline spin-crossover solid, which is hardly to process and difficult to use as a component for fabricating nano devices. In contrast to the above approaches, we are developing soft nanomaterials through programmed nanostructuring of metal complexes *via* covalent and non-covalent interactions. We employ one-, two-, and three-dimensional nanoarchitectures to construct well-defined coordination nanospace with spin-active metal complex as building blocks. By altering the size of building blocks, controlling their geometry and orientation, and directing their assembly, it is possible to engineer properties in unprecedented ways. Our strategy is promising for the development of a new family of spin-active nanomaterials whose functionalities and properties are heretofore unavailable in conventional crystalline metal complexes.

V-A-1 Molecular Design and Functions of Spin-Active Dendrimers

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Dendrimers are three-dimensional hyperbranched macromolecules that provide well-defined nanoscopic objects at the single molecular level. Unlike ordinary linear polymers, star-shaped polymers, and traditional branched polymers, dendrimers are characterized by their elaborate structure, which allows for precise control of their molecular size, shape, and the numbers and positions of functional groups. Recent studies on dendritic macromolecules have extended the scope of research from synthesis to applications for catalysts, photoactive and electronic materials, medicinal and biomedical materials, and other functional materials.

In this project, we are developing dendrimeric architecture for construction of novel metallodendrimers, whose metal sites are covalently linked in three-dimensional nanospace. By taking advantage of convergent approach, metallodendrimers with different generation numbers, different morphology, and different size are synthesized. These dendrimers provide a platform for the studies on magnetic interactions and cooperativity in spin crossover, among dendritic wedges within confined dendritic nanospace.

V-A-2 Molecular Design and Functions of Spin-Active One-Dimensional Nano-Channels

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In relation to project V-A-1, we are developing spin-active low-dimensional soft materials, in which metal sites are aligned through non-covalent interactions to assemble one-dimensional and two-dimensional arrays.

A series of triazole derivatives bearing water-soluble dendritic wedges with different generation numbers were synthesized as a bidentate ligand for coordination polymerization with iron(II). The rod-like rigid polynuclear chain appended with water-soluble dendritic wedges serves as a template for hybridization with mesoporous silicate. The hybrid consists of an iron(II) polynuclear chain that is spatially isolated within mesoporous channel, which thereby enables the investigation of magneto-optical properties at the single molecular level. Hybridized mesoporous silica thin film thus formed, due to its domain structure, functions as novel switching and high-density memory devices based on spin transition.

V-B Bioinorganic Chemistry and Structural Biology of Heme Proteins

One of research activities of my group is directed toward developing a rigorous, quantitative understanding of the biochemical function of heme proteins such as oxygenases, peroxidases and oxidases by characterization of their structural and functional properties. We use different experimental strategies including protein engineering, spectroscopic characterization of the molecular structure of the active centers, measurements of dynamics of substrates and inhibitor binding, and X-ray crystallography.

My current heme protein projects include (1) elucidation of the catalytic mechanism of heme oxygenase, one of the essential components of the heme catabolism and biosynthesis of carbon monoxide, a versatile physiological messenger molecule, (2) elucidation of the mechanism of controlling reactivity of hemoglobin and myoglobin, and (3) determination of heme sensing mechanism of Bach1, a heme-dependent transcription factor which regulates heme oxygenase gene expression. Effective clues to delineate the detailed active site structure have been obtained by X-ray crystallography, resonance Raman and magnetic resonance studies. The synergy of site-directed mutagenesis, structural biology, and spectroscopic techniques has revealed the specific roles of amino acids located in the active centers of heme proteins. Ligands and substrates binding measurements complement the structural data for our understanding functional properties displayed by heme proteins at the molecular level.

V-B-1 Compound I of Heme Oxygenase Can Not Hydroxylate Its Heme *meso*-Carbon

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[*J. Am. Chem. Soc.* **128**, 1090–1091 (2006)]

Heme oxygenase (HO) catalyzes heme catabolism through three successive oxygenation where the substrate heme itself activates O₂. It has been thought that the reactive species responsible for the first heme oxygenation, *meso*-hydroxylation, is the hydroperoxy-ferric heme intermediate (Fe–OOH) rather than an oxo ferryl porphyrin cation radical, so called compound I. A recent theoretical study (Kamachi *et al.*, *J. Am. Chem. Soc.* **127**, 10686 (2005)), however, proposed that compound I can oxidize its *meso*-carbon atom with the assistance of a bridging water molecule. In this communication, we have reported the first direct observation of compound I of a heme–HO-1 complex, generated by reaction of ferric–HO-1 with *m*-chloroperbenzoic acid. HO compound I slowly decays to compound II without producing any *meso*-hydroxylated products. It does react with guaiacol and thioanisole, however. Our findings unambiguously rule out involvement of compound I in the HO catalysis.

V-C Electronic Structure and Phase Stability of Bulk Metallic Glass

In this project, we have investigated the electronic structure and chemical bonding of the bulk metallic glasses, bulky multi-element amorphous alloys, experimentally by means of the synchrotron light photoemission spectroscopy and theoretically by the electronic structure calculation for their characteristic clusters, in order to understand the origin of their large glass forming ability from the microscopic point of view. Bulk metallic glasses show very high resistance against the crystallization of the super-cooled melt and a clear glass transition in spite of their thermodynamically metastable phase, and they have drawn much attention as new materials possessing useful engineering properties such as high mechanical strength, high corrosion resistance, good shaping ability, and soft-magnetic properties.

V-C-1 Electronic Structure of Bulk Metallic Glass $Zr_{55}Al_{10}Cu_{30}Ni_5$

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[*J. Electron. Spectrosc. Relat. Phenom.* **144-147**, 585–587 (2005)]

The electronic structure of a bulk metallic glass $Zr_{55}Al_{10}Cu_{30}Ni_5$ has been studied by means of photoelectron spectroscopy in order to understand the origins of its large glass formation ability and unique mechanical properties from the microscopic point of view. The valence-band photoelectron spectra show three bands ascribed to the Zr *4d*, Ni *3d* and Cu *3d* states. Remarkable feature of these bands is the highly-symmetric spectral shape with the high binding energy and narrow width in comparison with the *d* bands of the crystalline transition metals. This is attributed to the lack of the crystalline periodicity in the metallic glass as well as the reduction in the neighboring atoms to hybridize with those transition metals. High-resolution valence-band spectrum also reveals the intensity reduction near the Fermi level, which implies that the pseudo-gap in the electronic structure may be one of the important factors for the glass formation.

V-C-2 Free-Energy Estimation of the Zr-Ni-Al Bulk Metallic Glass from the Local Atomic Arrangements of the Relevant Crystals

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[*Mater. Trans.* **46**, 2791–2798 (2005)]

Free-energy of Zr-Ni-Al bulk metallic glass (BMG) was estimated by making full use of coordination clus-

ters in the relevant crystals. The clusters in the BMG were determined by using the BMG's experimentally determined radial distribution functions, and the electronic structure of the identified clusters was calculated by the DVX α cluster calculation. The local atomic arrangements in the Zr-Ni-Al BMG are found to be characterized by the prism clusters with Zr or Ni atom in their center and the Kasper polyhedrons about Al atoms. It was concluded, as a consequence of the present analysis, that the Zr-Ni-Al BMG are stabilized by the low internal energy of the constituent local atomic clusters assisted by the large entropy caused by the freedom in the bond-direction between the prism clusters and the Kasper polyhedrons.

V-C-3 Investigation of Stability of the Zr-Ni-Al Bulk Amorphous Phase from Local Atomic Arrangements of the Relevant Crystals

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[*J. Jpn. Soc. Powder Metallurgy* **53**, 100–106 (2006)]

Stability of the Zr-Ni-Al bulk metallic glass (BMG) was investigated by making full use of its relevant crystals. The local atomic arrangements (characteristic atomic clusters) commonly existing in the BMG and its relevant crystals were identified by the experimentally determined radial distribution functions. We found that the local atomic arrangements of the BMG were characterized by the prism clusters with a transition element, Zr or Ni, in their center and the Kasper polyhedron about an Al atom. Internal energy of these clusters was investigated by combinational use of the DVX α cluster calculation and the high-resolution photoemission spectroscopy. The prism clusters about the transition metal elements were confirmed to possess a low internal energy. We propose, as a consequence of present analysis, that the Zr-Ni-Al BMG is stabilized by the low internal-energy of the cluster and the large entropy caused by the freedom in the bond-direction between the clusters.

V-C-4 Electronic Structure of Zr-TM-Al (TM = Ni, Cu) Bulk Metallic Glasses

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[*J. Jpn. Soc. Powder Metallurgy* **53**, 107–110 (2006)]

The valence-band electronic structures of Zr-TM-Al (TM = Ni, Cu) bulk metallic glasses have been investigated by means of synchrotron-radiation photoelectron spectroscopy. Their valence-band spectra show Zr 4d-

Ni 3d- and Cu 3d-derived bands at the binding energies of 0.5, 2.0 and 3.6 eV, respectively. The Zr 4d-derived band becomes prominent around the excitation photon energy $h\nu$ of 40 eV. It is found that the wider the super-cooled liquid region $\Delta T_x = T_x - T_g$ (T_x : the crystallization temperature, T_g : the glass transition temperature), the larger the peak binding energy of the Zr 4d-derived band becomes. For the photoexcitation at $h\nu \sim 18$ eV, where the Zr 4d states less contribute to the spectrum, the spectral intensity reduces towards the Fermi level. This may imply the formation of a pseudogap in the sp bands. It is also found that the width of the pseudogap for the occupied states becomes wider as ΔT_x is increased. These spectral findings suggest that both the strength of the chemical bonding around Zr and the reduction in the electronic energy because of the pseudogap formation and the chemical bonding contribute to the large glass formation ability of the Zr-Cu-Al metallic glasses.

V-D Electronic Structures of Fe₂VAl Intermetallic Compound and Its Related Alloys

In this project, we have studied the electronic structures of the Heusler-type intermetallic compound Fe₂VAl and related alloys experimentally with use of the synchrotron light photoemission spectroscopy and theoretically by both the band structure calculation with a super cell and the cluster calculation, in order to clarify the mechanisms of its unusual transport properties and of the large enhancement of their thermoelectric properties. Fe₂VAl and related alloys have been received much attention because of not only the scientific interest in the anomalous transport properties at low temperatures but also their potential application for thermoelectric materials.

V-D-1 Surface and Bulk Electronic Structures of Heusler-Type Fe₂VAl

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[*J. Vac. Sci. Technol., A* **24**, 1464–1467 (2006)]

Surface and bulk electronic structures of Heusler-type ($L2_1$ -type) Fe₂VAl have been investigated by photoelectron spectroscopy, in particular, for the valence band and V 2p core level regions, in order to elucidate the changes in the valence band electronic structures for the surface and bulk regions. In the valence band spectrum, the intensity at the Fermi level E_F is increased for the surface-sensitive low photon energy excitation in comparison to the bulk-sensitive high photon energy excitation. It is also found that the intensity around a binding energy of 0.4 eV is enhanced for large photoelectron takeoff angles for the bulk-sensitive photoelectron spectrum. The V 2p core level spectrum shows a surface-derived shoulder structure on the low binding energy side of the main feature, which suggests that the valence electron concentration around V may be large in the surface layers in comparison to the bulk. These facts suggest that a pseudogap is formed around E_F in the

bulk electronic structure, as predicted by band calculations, and that it is destroyed in the surface layers by the V 3d states as well as the Fe 3d states emerging in mid pseudogap of the bulk electronic structure.

V-E Phase Dynamics under Ultra-High Pressures

Dynamics of phase transition under ultra-high pressures is investigated by using nanosecond time-resolved nonlinear Raman spectroscopy and laser shock compression. Shock wave induced by intense pulsed-laser irradiation can instantaneously generate ultra-high pressures (>1 GPa) and enable to monitor time-evolution of phase transition. By using nonlinear Raman spectroscopy such as stimulated Raman scattering and coherent anti-Stokes Raman scattering, change of molecular structure can be monitored.

V-E-1 Nanosecond Rapid Freezing of Liquid Benzene under Shock Compression Studied by Time-Resolved Coherent Anti-Stokes Raman Spectroscopy

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[*J. Chem. Phys.* **124**, 054501 (4 pages) (2006)]

Nanosecond time-resolved coherent anti-Stokes Raman spectroscopy is used to investigate the shock-induced liquid-solid phase transition and crystallization of liquid benzene. Temporal evolution of the Raman shift of the ring-breathing and C–H stretching mode is investigated. A metastable super-compressed state and a liquid–solid phase transition are observed under shock compression. Time-resolved Raman spectra reveal that liquid state is initially a metastable state and rapidly transforms to the solid state within 25 ns under shock compression at 4.2 GPa.

V-E-2 Time-Resolved Coherent Anti-Stokes Raman Scattering of Cyclohexane under Shock Compression

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[*Jpn. J. Appl. Phys.* **45**, 5817–5820 (2006)]

Time-resolved coherent anti-Stokes Raman scattering has been performed on cyclohexane under laser-driven shock compression of up to 2 GPa. The ring-breathing and C–C stretching mode exhibits blue shift, which agrees well with that obtained by static-compression experiments. The intensity increase of the shifted peak due to the propagation of the shock wave is observed. Shock velocity is obtained using anti-Stokes Raman scattering signal intensity ratio, and agrees well with that estimated from the measured particle velocity and Hugoniot.

V-F Pyrrole-Based Molecular Assemblies and Supramolecular Structures

An important class of naked-eye sensors are synthetic receptors that permit anionic guest species to be seen by visual means or *via* changes in the electronic absorption or fluorescent spectral properties. Among the various artificial host molecules reported to date, pyrroles incorporated into macrocycles are particularly attractive because they behave as essential binding units due to the presence of polarized NH sites. Although less well studied, acyclic pyrrole derivatives often potentially have even more advantages. This is because they can form the complexes with anions via the synthetic attachment of additional recognition units such as amide NH, or simply because they are easily to make their macrocyclic systems.

On the other hand, metal ion coordination enables organic ligands to form versatile discrete or infinite architectures, such as wire structures and nanospace materials, with potential applications in catalysis, optics, and biosensing. Recently, nanoscale morphologies based on coordination polymers have been reported to exist as spherical and fibrous structures. Of the coordinating ligands, dipyrrens (dipyrromethenes), consisting of two pyrroles with an sp^2 -*meso* position, are essential π -conjugated *bidentate monoanionic* ligands for metal ions in natural and artificial systems. Therefore, dipyrrens are promising planar scaffoldings for self-assemblies and would give neutral coordination oligomers and, which, in combination with various spacer units, could be used to fabricate fine-tuned nanoscale morphologies using bridging metal cations.

From the above background, we are focusing on development of nanoarchitectures based on metal coordination of dipyrren oligomers as well as efficient anion binding systems of acyclic oligopyrroles.

V-F-1 Dipyrrolyldiketone Difluoroboron Complexes: Novel Anion Sensors with C–H...X[−] Interactions

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[*Chem. Eur. J.* **11**, 5661–5666 (2005)]

1,3-Dipyrrolyl-1,3-propanediones, synthesized from pyrroles and malonyl chloride, form BF₂ complexes, a new class of naked-eye sensors for halide and oxoanions. Association mode with the interactions of both the pyrrolyl NH and bridging CH protons for anion was confirmed by ¹H NMR chemical shifts in CD₂Cl₂ and supported by theoretical study. Binding constants (K_a) were estimated at 8.1×10^4 , 2.0×10^3 , 3.3×10^2 , 1.3×10^4 , and 80 M^{-1} for F[−], Cl[−], Br[−], H₂PO₄[−], and HSO₄[−] by UV/vis absorption spectral changes in CH₂Cl₂. Augmentation of K_a compared to dipyrrolylquinoxaline for H₂PO₄[−] is much larger than those for other anions. F[−] quenches the emission almost completely, contrasted with other anions, detected by fluorescence spectrum as well as naked-eye. In the case of the chloride anion complex, the formation of Cl[−]-bridged 1-D networks, in which anion is associated with two BF₂ complexes, is observed in the solid state.

V-F-2 CH...Anion Interaction in BF₂ Complexes of C₃-Bridged Oligopyrroles

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[*J. Org. Chem.* **71**, 2389–2394 (2006)]

Alkyl-substituted derivatives of 1,3-dipyrrolyl-1,3-propanedione BF₂ complexes, the efficient receptors for halide and oxoanions using bridging CH as well as

pyrrole NH, are reported. BF₂ complexes with only one pyrrole NH interaction site, which exhibit less affinities than the basic structures, bind anions tightly, inferred by UV/vis absorption spectral changes, compared to the derivatives with an alkyl group at the bridging carbon or two pyrrole nitrogen sites. Using ¹H NMR and theoretical studies for anion complexes of N-blocked and N-lacked receptors, bridging CH (and one β -CH in N-blocked) as well as pyrrole NH is found to interact with anions.

V-F-3 BF₂ Complex of Fluorinated Dipyrrolyldiketone: A New Class of Efficient Receptor for Acetate Anions

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[*Inorg. Chem.* **45**, 8205–8210 (2006)]

β -Fluorinated derivative of 1,3-dipyrrolyl-1,3-propanedione BF₂ complex has been prepared from 3,4-difluoropyrrole and malonyl chloride followed by treatment with BF₃·OEt₂. Despite the simple, acyclic, and neutral structure, β -fluorinated receptor exhibits efficient 1:1 binding for anions in CH₂Cl₂ using bridging CH and pyrrole NH as interaction sites. Binding constant (K_a) for acetate (CH₃CO₂[−]), associated more effectively compared to the anions like F[−], Cl[−], Br[−], H₂PO₄[−], and HSO₄[−], is estimated as $9.6 \times 10^5 \text{ M}^{-1}$, *ca.* 9-times augmented in comparison with that of β -H derivative ($1.1 \times 10^5 \text{ M}^{-1}$). UV/vis and fluorescence spectral changes of the receptors elucidate the effective recognition of an amino acid such as phenylalanine in anionic form, also supported by CD spectral changes with mirror images by L- and D-isomers. Furthermore, in the solid state, BF₂ complex of β -F receptor provides Cl[−]-bridged supramolecular networks, and, in sharp contrast, deprotonated “anionic” self-assembled structures by F[−] binding.

V-F-4 Dipyrin-Porphyrin Hybrids: Potential π -Conjugated Platform to Fabricate Coordination Oligomers

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[*Chem. Lett.* **34**, 1150–1151 (2005)]

Bis-dipyrin-appended porphyrin derivatives are synthesized and exhibited complexation at the two dipyrin sites with BF_2 and $\text{Rh}(\text{CO})_2$. Treatment with $\text{Zn}(\text{OAc})_2$ is found to show the MALDI-TOF-MS suggesting the formation of dimer (corresponding to $2 \times$ dipyrin-porphyrin hybrid + $2 \times \text{Zn}^{2+}$) as a major product and trimetric and tetrametric structures as traces, which infers that the dipyrin moieties behave as potential scaffolds for supramolecular coordination polymers.

V-F-5 Nanoscale Spherical Architectures Fabricated by Metal Coordination of Multiple Dipyrin Moieties

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[*J. Am. Chem. Soc.* **128**, 10024–10025 (2006)]

Phenylethynyl-bridged dipyrin “dimers” have been prepared by cross-coupling reactions of bromobenzaldehydes and diethynylbenzenes followed by condensation with pyrrole and a subsequent DDQ oxidation. The dipyrin dimers performed Zn^{II} complexation in THF, detected by UV/vis and ^1H NMR spectral changes. The coordination oligomers, according to the spacer units, provided the submicrometer-scale colloidal spherical objects observed by DLS measurements in solution and SEM, TEM, and optical microscopy on the substrate. Using mixture of THF and water, unique morphologies, such as hemispheres and bell-shaped and “golf ball”-like architectures, were observed. The coordination oligomers have emission maxima at 510–515 nm in THF, which can be ascribed to the Zn^{II} -bisdipyrin moieties, and give fluorescent spherical objects with emission at 532–543 nm in the solid state by assembly from THF. In contrast, addition of a 1:1 mixture of $\text{Zn}(\text{OAc})_2$ and $\text{Cu}(\text{OAc})_2$ into a THF solution of dipyrin dimer resulted in quenching of emission from the Zn^{II} -dipyrin units similarly to the case of the single Cu^{II} complex possibly due to intramolecular energy transfer.