

VIII-H Creation of Novel Functional Nano Materials Based on Proton-Coupled Electronic Properties

Dynamics of molecules and ions in “coordination nano-space” are acted by characteristic nano-fields such as intermolecular interaction, coulomb interaction, catalytic action, *etc.* This project is to reveal a basic principle of an unusual nano-field acting on coordination space, and to create the nano space where the energy conversions can be easily operated. In particular, we aim at the construction of coordination nano space system which is able to control a series of energy operations such as generation, separation, storage, material conversion of an energy molecule H₂, or electron/ion transport. In this year, we have explored a novel hydrogen-energy functional coordination nano-space by using proton-coupled redox and electron-proton interaction. In the present project, we will create new 1) hydrogen-storage nano-materials, 2) highly proton-conductive coordination polymers, 3) highly electron-proton conductive materials, *etc.*

VIII-H-1 Most Stable Metallic Phase of the Mixed-Valence MMX-Chain, Pt₂(dtp)₄I (dtp: C₂H₅CS₂⁻) in Purely *d*-Electronic Conductors Based on the Transition-Metal Complex

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The electrical resistivity and X-ray oscillation photograph measurements for an MMX-Chain complex, Pt₂(dtp)₄I (dtp = C₂H₅CS₂⁻) under high pressure were performed. We observed the most stable metallic phase ($T_{MI} = 70$ K, under 2.2 GPa) in the 1-D purely *d*-electronic conductors and pressure-induced metal-insulator transition including structural phase transition at 3.0 GPa.

VIII-H-2 Direct Determination of Low-Dimensional Structures: Synchrotron X-Ray Scattering on One-Dimensional Charge-Ordered MMX-Chain Complexes

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A powerful method to determine the hidden structural parameters in functional molecules has been developed. Local valence arrangements that dominate the material properties are sometimes not three-dimensionally ordered. This method that comprises diffuse X-ray scattering and resonant X-ray scattering is suitable in such cases. Using this method, we present clear evidence of the low-dimensional valence arrangement in two halogen-bridged one-dimensional metal complexes, so-called MMX chains. This family allows us to control many physical and structural parameters by chemical substitution of bridging halogen, counterions, or metal

ions, and one of our samples carries an unusual metallic phase. It is demonstrated with this complex that the present method makes it possible to have microscopic insight to low-dimensionally ordered systems.

VIII-H-3 Pressure-Induced Metal–Semiconductor–Metal Transitions in an MMX-Chain Complex, Pt₂(C₂H₅CS₂)₄I

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The electrical conductivity and X-ray diffraction measurements under high pressure up to 2.5 GPa were performed for a highly-conductive halogen-bridged binuclear-metal mixed-valence complex (the so-called MMX chain), Pt₂(C₂H₅CS₂)₄I. It exhibited pressure-induced metal-semiconductor-metal transitions at 0.5 and 2.1 GPa. The X-ray diffuse scatterings were observed at $k = n + 0.5$ (n : integer) under ambient pressure, which are derived from the charge-density-wave (CDW: ...Pt²⁺–Pt²⁺...I–Pt³⁺–Pt³⁺–I...) fluctuation in the MMX chain. Above 0.5 GPa where the pressure-induced metal-semiconductor transition occurred, these scatterings disappeared. The electronic phases under high pressure (P) were found to be attributable to the metallic averaged-valence state (AV: –Pt^{2.5+}–Pt^{2.5+}–I–Pt^{2.5+}–Pt^{2.5+}–I–) with CDW fluctuation for $P < 0.5$ GPa, semi-conducting charge-polarization state (CP: ...Pt²⁺–Pt³⁺–I...Pt²⁺–Pt³⁺–I...) for $0.5 < P < 2.1$ GPa, and metallic AV state for $P > 2.1$ GPa. The electronic state of Pt₂(C₂H₅CS₂)₄I is very sensitive to pressure, implying that phase competition among the CP, CDW and AV phases is present in the MMX chain.

VIII-H-4 Synthesis of a One-Dimensional Metal-Dimer Assembled System with Interdimer Interaction, M₂(dtp)₄ (M = Ni, Pd; dtp = Dithiopropionato)

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A metal-dimer assembled system, $M_2(dtp)_4$ ($M = Ni, Pd$; $dtp =$ dithiopropionate, $C_2H_5CS_2^-$) was synthesized and analyzed by X-ray single-crystal diffraction method, UV-Vis-Near-IR of solutions and solid state diffuse reflectance spectroscopies, and electrical conductivity measurement. The structures exhibit one-dimensional metal-dimer chains of $-M_2(dtp)_4-M_2(dtp)_4-M_2(dtp)_4-$ with moderate interdimer contact. These complexes are semiconducting or insulating, which is consistent with the fully filled d_z^2 band of $M^{II}(d^8)$. Interdimer metal-metal distances were 3.644(2) Å in $Ni_2(dtp)_4$ and 3.428(2) Å in $Pd_2(dtp)_4$, each of which is marginally longer than twice the van der Waals radius of the metal. Interdimer charge-transfer transitions were nevertheless observed in diffuse reflectance spectra. The origin of this transition is considered to be due to an overlap of two adjacent d_{σ^*} orbitals which spread out more than d_z^2 orbital due to the antibonding d_{σ^*} character of the $M(d_z^2)-M(d_z^2)$. The $Ni_2(dtp)_4$ exhibited an interdimer charge transfer band at relatively low energy region, which is derived from the Coulomb repulsion of $3d_{\sigma^*}$ orbital of Ni.

VIII-H-5 Galvanostatic Transient Studies on Copper Coordination Polymer under Hydrogen Absorption

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Hydrogen electrode reaction (HER) was investigated for a copper coordination polymer, catena- $\mu-N,N'$ -bis(hydroxyethyl)dithiooxamidatocopper(II) (CuCP) by galvanostatic transient measurements using a palladium cathode. Individual steps in the Volmer-Tafel reaction were successfully observed for the colloidal CuCP in alkaline solution under hydrogen absorption. The Volmer step was found to be promoted with CuCP and its hydrogen-absorbed polymer (CuCPH) from shorter decay times in transient curves and smaller overpotentials in Tafel plots. In contrast, the inhibition of the Tafel step was observed, which is due to the larger overpotentials. Difference in reducibility between the polymers and plausible reduction mechanisms is discussed.