

VII-D Nano-Sciences of Advanced Metal Complexes

Recently, nano-sciences or nano-technologies have been attracting much attention because they show very interesting physical properties based on the non-linearity and quantum effect. There are two methods to obtain the nano-size materials, that is, "top-down" and "bottom-up." The top-down method such as laser abrasion has a limitation to make particles with less than 100 nm. On the other hand, the bottom-up method is promising to control the nano-size since the chemical reactions are available. However, the researches based on the bottom-up methods are rare and such methods have not been accomplished so far. There are three types of the target materials such as inorganic compounds, organic compounds, and metal complexes. The inorganic compounds easily take three-dimensional bulk structures. The organic compounds easily take 0- and 1-dimensional bulk materials. Therefore, neither inorganic nor organic compounds are suitable for the nano-sciences. On the other hand, the metal complexes easily take nano-size clusters where they are surrounded with the organic ligands. Therefore, the nano-sciences of the advanced metal complexes are most promising. As for the non-linearity, we focus on the gigantic third-order optical non-linearity. As for the quantum effect, we focus on the single-molecule magnets, nano-wire molecule-magnets, and nano-network molecule-magnets.

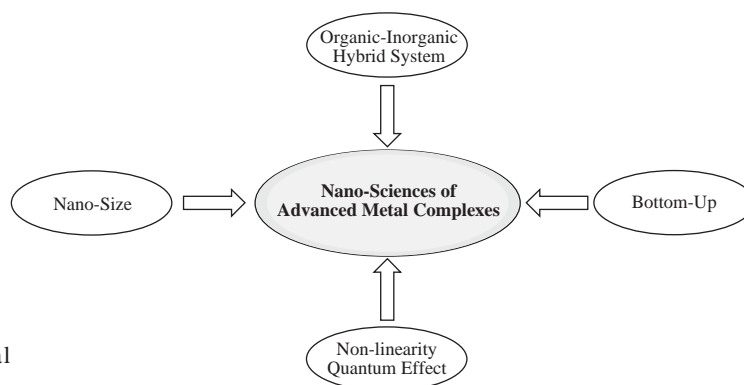


Figure 1. Nano-sciences of advanced metal complexes.

VII-D-1 Tuning of Electronic Structures of Quasi-One-Dimensional Bromo-Bridged Ni(III) Complexes with Strong Electron-Correlation by Doping of Co(III) Ions, $[\text{Ni}_{1-x}\text{Co}_x(\text{chxn})_2\text{Br}]\text{Br}_2$

YAMASHITA, Masahiro¹; YOKOYAMA, Kohei²; FURUKAWA, Sachie²; MANABE, Toshio²; ONO, Takashi²; NAKATA, Kazuya²; KACHITERAJIMA, Chihiro²; IWAHORI, Fumiyasu²; ISHII, Tomohiko²; MIYASAKA, Hitoshi²; SUGIURA, Ken-ichi²; MATSUZAKI, Hiroyuki³; KISHIDA, Hideo³; OKAMOTO, Hiroshi³; TANAKA, Hisaaki⁴; MARUMOTO, Kazuhiro⁴; ITO, Hiroshi⁴; KURODA, Shin-ichi⁴

(¹IMS and Tokyo Metropolitan Univ.; ²Tokyo Metropolitan Univ.; ³Univ. Tokyo; ⁴Nagoya Univ.)

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The Ni(III) complexes doped by Co(III) ions, $[\text{Ni}_{1-x}\text{Co}_x(\text{chxn})_2\text{Br}]\text{Br}_2$ have been synthesized by electrochemical oxidation methods. The single crystal reflectance spectrum of $x = 0.118$ shows an intense CT band about 0.5 eV, which is lower than that of $[\text{Ni}(\text{chxn})_2\text{Br}]\text{Br}_2$ (1.3 eV). The single-crystal electrical conductivities at room temperature of these compounds increase with increase of the amounts of doping of Co(III) ions. In the ESR spectra, peak-to-peak line widths at room temperature change about 600 G in $[\text{Ni}(\text{chxn})_2\text{Br}]\text{Br}_2$ to 200 G in $x = 0.118$. Such a large x dependence of line widths seems to be ascribed to the increasing contribution from the increasing Curie spins which have smaller

line width. Therefore, we have succeeded in tuning the electronic structures of quasi-one-dimensional bromo-bridged Ni(III) complexes with strong electron-correlations by doping Co(III) ions.

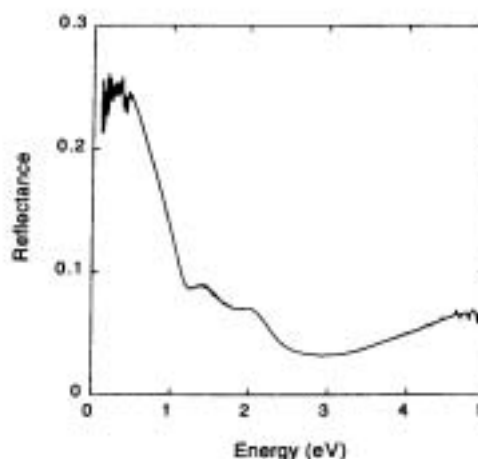


Figure 1. Single-crystal reflectance spectrum of $[\text{Ni}_{0.882}\text{Co}_{0.118}(\text{chxn})_2\text{Br}]\text{Br}_2$.

VII-D-2 Angle-Resolved Photoemission Study of the MX-Chain Compound $[\text{Ni}(\text{chxn})_2\text{Br}]\text{Br}_2$: Spin-Charge Separation in Hybridized *d-p* Chains

FUJIMORI, Shin-ichi¹; INO, Akihiro¹; OKANE, Tetsuo¹; FUJIMORI, Atsushi¹; OKADA, Kozo²; MANABE, Toshio³; YAMASHITA, Masahiro⁴;

KISHIDA, Hideo⁵; OKAMOTO, Hiroshi⁵
 (¹Spring-8; ²Okayama Univ.; ³Tokyo Metropolitan Univ.; ⁴IMS and Tokyo Metropolitan Univ.; ⁵Univ. Tokyo)

[*Phys. Rev. Lett.* **88**, 247601-1 (2002)]

Angle-resolved photoemission experiments have been carried out for a quasi-one-dimensional (1D) MX-chain compound $[\text{Ni}(\text{chxn})_2\text{Br}]\text{Br}_2$, which shows a gigantic nonlinear optical effect. A "band" having about 500 meV energy dispersion is found in the first half of the Brillouin zone, but disappears at $kb/\pi \sim 1/2$. These spectral features are well reproduced by the d - p chain model with a small charge-transfer energy Δ compared with that in 1D Cu-O compounds. It is proposed that this smaller Δ is the origin of the absence of clear spin-charge separation in the photoemission spectra and the strong nonlinear optical effect.

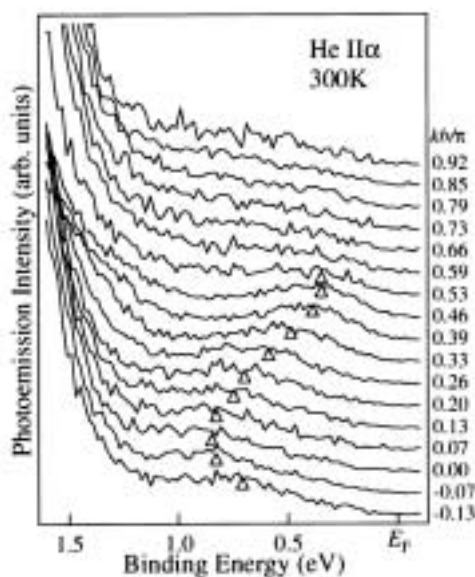


Figure 1. ARPES spectra of $[\text{Ni}(\text{chxn})_2\text{Br}]\text{Br}_2$.

VII-D-3 ESR Detection of Induced Spin Moments in Halogen-Bridged Mixed-Metal Complexes $\text{Ni}_{1-x}\text{Pd}_x(\text{chxn})_2\text{Br}_3$

TANAKA, Hisaaki¹; MARUMOTO, Kazuhiro¹; KURODA, Shin-ichi¹; MANABE, Toshio²; YAMASHITA, Masahiro³
 (¹Nagoya Univ.; ²Tokyo Metropolitan Univ.; ³IMS and Tokyo Metropolitan Univ.)

[*J. Phys. Soc. Jpn.* **71**, 1370 (2002)]

ESR measurements have been performed on single crystals of the quasi-one-dimensional halogen-bridged mixed-metal complexes, $\text{Ni}_{1-x}\text{Pd}_x(\text{chxn})_2\text{Br}_3$, where on-site Coulomb interaction (Ni^{3+} case) and electron-phonon interaction (Pd^{2+} - Pd^{4+} case) are competing with each other. Monotonic decrease of principal g -values from $g(\text{Ni})_{\text{max}} = 2.118$ to $g(\text{Pd})_{\text{max}} = 2.113$ was observed as x increases. This indicates that the magnetic Pd^{3+} ions with smaller g -value than that of Ni^{3+} are induced from non-magnetic Pd^{2+} - Pd^{4+} chain, which is

consistent with the previous observed spin susceptibility enhancement in this system. In addition, monotonic decrease of the ESR linewidth is observed as x increases indicating the contribution of Pd^{3+} ions with longer spin-lattice relaxation time T_{1D} , which is supported by using isomorphous chlorine complexes $\text{Ni}(\text{chxn})_2\text{Cl}_3$ and $\text{Pd}(\text{chxn})_2\text{Cl}_3$.

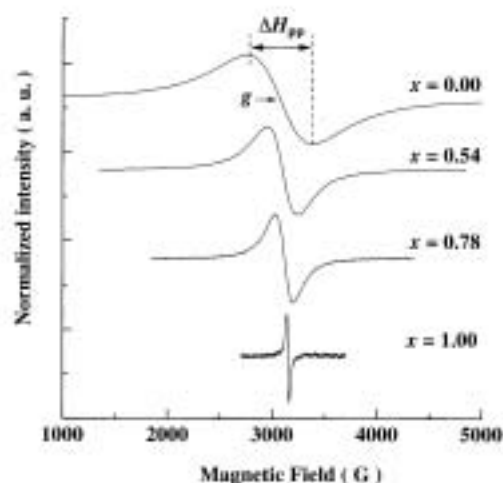


Figure 1. First derivative ESR spectra of single crystalline $\text{Ni}_{1-x}\text{Pd}_x(\text{chxn})_2\text{Br}_3$.

VII-D-4 A Chemical Modification of a Mn_{12} Single-Molecule Magnet by Replacing Carboxylate Anions with Diphenylphosphate Anions

KURODA-SOWA, Takayoshi¹; FUKUDA, Satoshi¹; MAEKAWA, Masahiko¹; MUNAKATA, Megumu¹; MIYASAKA, Hitoshi²; YAMASHITA, Masahiro³
 (¹Kinki Univ.; ²Tokyo Metropolitan Univ.; ³IMS and Tokyo Metropolitan Univ.)

[*Chem. Lett.* 682 (2002)]

Diphenylphosphate anion can replace with benzoate anions of $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CPh})_{16}(\text{H}_2\text{O})_4]$ to afford a novel Mn_{12} single-molecule magnet (SMM) with mixed bridging ligands.

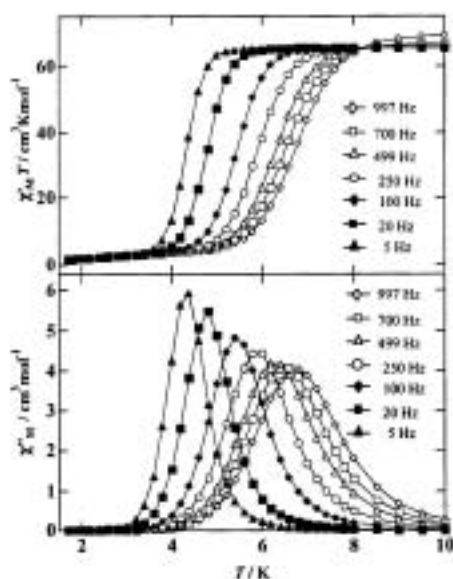


Figure 1. AC magnetic susceptibility data in the form of $\chi'_{M}T$ -T (top) and $\chi''_{M}T$ -T (bottom) plots.

VII-D-5 Construction of a One-Dimensional Chain Composed of Mn_6 Clusters and 4,4'-Bipyridine Linker: The First Step for Creation of "Nano-Dots-Wires"

NAKATA, Kazuya¹; SUGIMOTO, Kunihisa²;
ISHII, Tomohiko¹; SUGIURA, Ken-ichi¹;
YAMASHITA, Masahiro³
(¹Tokyo Metropolitan Univ.; ²Rigaku Co. Ltd.; ³IMS
and Tokyo Metropolitan Univ.)

[Chem. Lett. 658 (2002)]

Treatment of a mixed-valence Mn_6 cluster, $[Mn_6O_2(t-BuCO_2)_{10}(t-BuCO_2H)_4]$ (1), with 4,4'-bipyridine (bpy) in dichloromethane/1,2-dichloroethane solution gave a one-dimensional polymer chain compounds, $[Mn_6O_2(t-BuCO_2)_{10}(t-BuCO_2H)_2(bpy)]$ (2), in which the present cluster core was maintained as a building block.

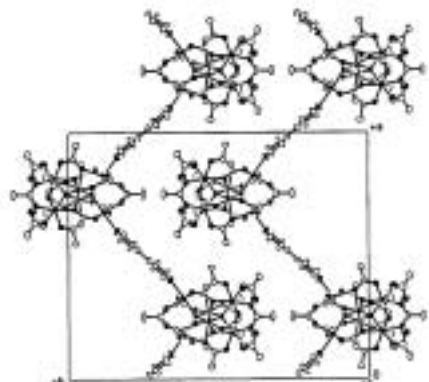


Figure 1. Packing diagram of the 1D chain compound projected along the c axis.

VII-D-6 Framework Engineering by Anions and Porous Functionalities Cu(II)/4,4'-bpy Coordination Polymers

NORO, Shin-ichiro¹; KITAURA, Ryo¹; KONDO, Mituru¹; KITAGAWA, Susumu¹; ISHII, Tomohiko²; MATSUZAKA, Hiroyuki²;
YAMASHITA, Masahiro³
(¹Kyoto Univ.; ²Tokyo Metropolitan Univ.; ³IMS and Tokyo Metropolitan Univ.)

[J. Am. Chem. Soc. 124, 2568 (2002)]

A combination of framework-builder (Cu(II) ion and 4,4'-bipyridine (4,4'-bpy) ligand) and framework regulator (AF_6 type anions; A = Si, Ge, and P) provides a series of novel porous coordination polymers. The highly porous coordination polymers $\{[Cu(AF_6)(4,4'-bpy)_2]_8H_2O\}_n$ (A = Si (1a.8H₂O), Ge (2a.8H₂O)) afford robust 3-dimensional (3-D), microporous networks (3D Regular Grid) by using AF_6^{2-} anions. The channel size of these complexes is *ca.* $8 \times 8 \text{ \AA}^2$ along the c -axis and $6 \times 2 \text{ \AA}^2$ along the a -axis or b -axis. When compounds 1a.8H₂O or 2a.8H₂O were immersed in water, a conversion of 3-D networks (1a.8H₂O or 2a.8H₂O) to interpenetrated network $\{[Cu(4,4'-bpy)_2(H_2O)_2] \cdot AF_6\}_n$ (A = Si(1b) and Ge(2b)) (2D-interpenetration) took place. The 2-D interpenetrated network 1b shows unique dynamic anion-exchange properties, which accompany drastic structural conversions. When a PF_6^- monoanion instead of AF_6^{2-} dianion was used as the framework-regulator with another co-counteranion (coexistent anions), porous coordination polymer with various types of frameworks. Interestingly, these Cu(II) frameworks are rationally controlled by counteranions and selectively converted to other frameworks.

VII-D-7 New Microporous Coordination Polymer Affording Guest-Coordination Sites at Channel Walls

NORO, Shin-ichiro¹; KITAGAWA, Susumu¹;
YAMASHITA, Masahiro²; WADA, Tatsuo³
(¹Kyoto Univ.; ²IMS and Tokyo Metropolitan Univ.; ³RIKEN)

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Utilization of a metalloligand, $\{[Cu(2,4-pydca)_2(H_2O)] \cdot 2Et_3NH\}$ (1) (2,4-pydca = pyridine-2,4-dicarboxylate), as a building unit provides a novel porous coordination polymer, $\{[ZnCu(2,4-pydca)_2(H_2O)_3(DMF)] \cdot DMF\}_n$ (2), in which the Zn(II) ion at the node of the network acts as a linker and the Cu(II) ion in the channel wall is available for guest-coordination.