Magnetic Resonance Studies for Functional Molecular-Based Solids

Department of Materials Molecular Science
Division of Electronic Properties

NAKAMURA, Toshikazu
Associate Professor
[t-nk@ims.ac.jp]

Education

1987	B.S. Kyoto University
1995	D.S. Kyoto University

Professional Employment

1992	Assistant Professor, Gakushuin University
1998	Associate Professor, Institute for Molecular Science
2003	Associate Professor, The Graduate University for Advanced Studies

Member
Secretary
ABE, Hitomi
YAMASAKI, Yumi

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Magnetic resonance measurements are advantageous for studying fundamental electronic properties and for understanding the detailed electronic structures of molecular based compounds. Developing an understanding of the electronic phases and functionality of these materials enables us to perform systematic investigations of low-dimensional, highly-correlated electron systems and functional materials. Competition between the electronic phases in molecular-based conductors has attracted much attention. The investigations of such electronic phases by magnetic resonance measurements are important to understanding unsolved fundamental problems in the field of solid state physics, and to explore novel functionalities in the field of material science.

In this study, we performed broad-line NMR and ESR measurements on molecular-based conductors to understand electron spin dynamics and functionality in low-temperature electronic phases.

Figure 1. Solid state broad-line NMR system (above). Multi-frequency pulsed ESR system (below).

Selected Publications

- P. Pandit, K. Yamamoto, T. Nakamura, K. Nishimura, Y. Kurashige, T. Yanai, G. Nakamura, S. Masaoka, K. Furukawa, Y. Yakiyama, M. Kawanoe and S. Higashibayashi, "Acid/Base-Regulated Reversible Electron Transfer Disproportionation of N-N Linked Bicarbazole and Biacridine Derivatives," *Chem. Sci.* **6**, 4160–4173 (2015).
- M. Yoshida, M. Kondo, T. Nakamura, K. Sakai and S. Masaoka, "Three Distinct Redox States of an Oxo-Bridged Dinuclear Ruthenium Complex," *Angew. Chem., Int. Ed.* **53**, 11519–11523 (2014).

1. Microscopic Evidence of a Metallic State in the One-Pot Organic Conductor, Ammonium Tetrathiapentalene Carboxylate

We performed magnetic resonance investigation, including solid-state broad line NMR and high-field ESR measurements, of the π-extended self-doped organic conductor $(TTPCOO)_2[(NH_4^{+1})_{1-x}(NH_3^0)_x]$, and compared the results with those of first-generation $(TTFCOO)[(NH_4^{+1})_{1-x}(NH_3^0)_x]$. The observed principal values of the ESR g-tensor indicate that both salts have electron spins on TTF and TTP cation radical mainframe parts. In $(TTFCOO)[(NH_4^{+1})_{1-x}(NH_3^0)_x]$, the TTF forms a 1D uniform stacking structure, and the system is a narrow-gap semiconductor. The electron spin demonstrates 1D spin-diffusive behavior, which may be why this system is a semiconductor. On the other hand, in the π-extended system, TTPCOO, the uniaxial anisotropy of the g-tensor indicates a 2D isotropic structure such as a herring-bone-like or parallel cross like donor arrangement. The π-extended system should reduce the electronic correlation that stabilizes the metallic state. As a result, NMR-relaxation demonstrates the Korringa-like temperature dependence, and the ESR linewidth follows the Elliot mechanism. These facts are apparent evidence of a stable metallic state (itinerant electron spins are present). We demonstrate that advanced magnetic resonance measurements can effectively clarify the intrinsic characteristics and functionality of novel materials. Moreover, this one-pot process for synthesizing organic (semi-) conductors enables large-scale high-volume synthesis in a short time. Our next goal is to realize a one-pot functional organic system such as superconducting, ferromagnetic, or ferroelectric materials.

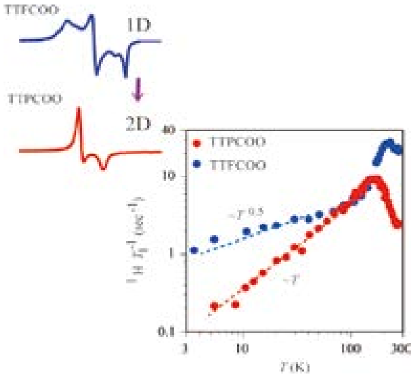

Figure 2. Metallic state in one-pot organic conductor, an ammonium tetrathiapentalene carboxylate based system is found. High-field ESR spectra showed a 2D isotropic structure such as a herring-bone-like donor arrangement. This is unlike the 1D ammonium tetrathiafulvalene carboxylate system. NMR-relaxation and the ESR linewidth provide strong evidence of a stable metallic state in the ammonium tetrathiapentalene carboxylate system.

2. Charge Ordering in Oxo-Bridged Dinuclear Ruthenium Mixed-Valence Complex by Magnetic Resonance Investigation

Solid-state broad line ^{1}H-NMR was carried out for an oxo-bridged dinuclear ruthenium mixed-valence complex. A pronounced peak in the ^{1}H-NMR T_1^{-1} was observed around 33 K. The frequency independence of the peak temperature of T_1^{-1} indicates that this anomaly is not a crossover phenomenon but a phase transition. This 33 K anomaly is a transition from an averaged-valence state to a trapped-valence state in $[RuORu]^{5+}$; that is, the averaged-valence $Ru^{3.5+}ORu^{3.5+}$ spontaneously breaks symmetry into $Ru^{3+}ORu^{4+}$ below 33 K. In other word, the electronic charge freedom is cooperatively frozen at 33 K. The observed abrupt decrease in T2 also indicates internal charge separation ($Ru^{3+}ORu^{4+}$). Because the 33 K anomaly is cooperative phenomena, the Ru^{3+} and Ru^{4+} charge configuration must be regularly arranged by necessity in the phase transition. Considering the crystal structure symmetry, one possible schematic charge configuration within the ac-plane is shown in Figure 3. Of course, this is mere speculation, and detailed structural measurements at a synchrotron radiation facility are required. Note also that the ruthenium-equivalent sites are connected by an inversion center in the $[RuORu]^{5+}$ complex, so the charge order state should be antiferroelectric. For applicable use, ferroelectric and/or multiferroic materials are desired. The development of dinuclear complexes with lower symmetry and stronger inter-molecular interactions is a good next step, and further investigations are already underway. However, we emphasize on the basis of this investigation that mixed-valence metal complexes are excellent candidates for electronic device materials.

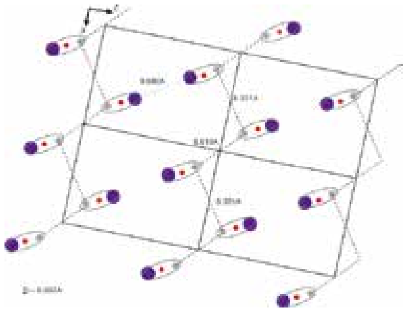

Figure 3. Possible schematic charge configuration within the ac-plane below 33 K.

References

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2) T. Nakamura, M. Yoshida, M. Kondo and S. Masaoka, submitted.