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

Award

2017	The 22nd Outstanding Paper Award of the Physical Society of Japan

Member
IMS Research Assistant Professor
ASADA, Mizue
Secretary
YAMASAKI, Yumi

Keywords Organic Conductor, Electron Spin Resonance (ESR), Nuclear Magnetic Resonance (NMR)

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

- T. Nakamura, K. Furukawa, T. Terauchi and Y. Kobayashi, "Microscopic Evidence of a Metallic State in the One-Pot Organic Conductor, Ammonium Tetrathiapentalene Carboxylate," *Phys. Status Solidi RRL* **9**, 480–484 (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. Magnetic Investigation of Iodine-Doped COF (Covalent-Organic-Framework)

COF materials are pours crystalline materials, which attract much attention because of their functionalities. We investigated the photoconduction mechanism by time-resolved ESR.[1)] Recently a two-dimensional (2D) crystalline covalent organic framework (sp^{2}c-COF) that is fully π-conjugated and constructed from all sp^2-carbons by C=C condensation reactions of tetrakis(4-formylphenyl)pyrene and 1,4-phenylenediacetonitrile.[2)] The sp^{2}c-COF can be chemically oxidized with iodine, and the generated radical spins are on the pyrene skeletons. To investigate the electronic states down to low-temperatures, we performed ESR and SQUID measurements for the 2D sp^{2}c-COF. An ESR signal appeared at g = 2.003, just after iodine doping. The ESR linewidth and g-values were almost constant regardless of the doping level. The ESR linewidth of 1.3 Gauss is narrow. The significant increase of ESR intensity indicates that high concentration spin injection realized. The χ_{spin} determined by ESR and SQUID measurements indicates the existing spin freedom down to the low temperature. Curious low-temperature behavior of spin system is also discussed.

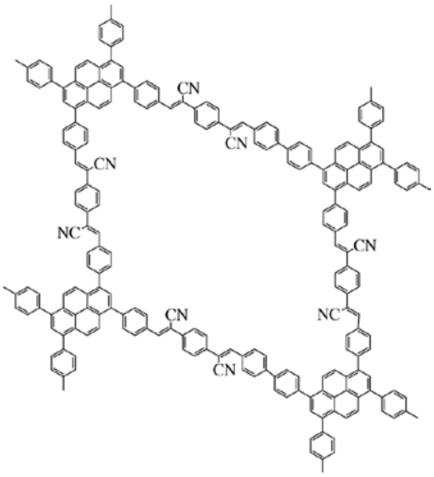

Figure 2. Molecular structure of sp^{2}c-COF.

2. Low-Temperature Electronic Phases in One-Dimensional Organic Conductors (TMT*C*F)$_2$*X*

One-dimensional conductors based on (TMT*C*F)$_2$*X* (*C* = S, Se) are some of the most extensively studied materials among organic conductors. They possess various ground states including the spin-singlet (SS), commensurate antiferromagnetic state (C-AF), incommensurate spin density wave (IC-SDW) and superconductivity (SC), with applied pressures or counter anions, *X*. Moreover, findings of charge-ordering (CO) and related phenomena in (TMTTF)$_2$*X* have attracted significant recent attention.

(TMTTF)$_2$*M*F$_6$ shows successive phase transitions as the temperature decreases. In paramagnetic region, these salts undergo a charge-ordering phase transitions. With synchrotron x-ray diffraction, we directly observed a slight structural difference owing to the effect of charge-order transition between two TMTTF molecules in a dimer for (TMTTF)$_2$PF$_6$.[3)] The charge distribution is estimated as 0.20e, which is close to that observed in NMR.

(TMTTF)$_2$Br undergoes antiferromagnetic transition at 16 K (T_{N}). But it is located on the proximity between C-AF and IC-SDW phase in the generalized phase diagram. To understand the electronic states on the boundary region between the commensurate antiferromagnetic phase and the incommensurate spin-density-wave (IC-SDW) phase in the generalized phase diagram for 1D organic conductors, we performed antiferromagnetic resonance (AFMR) and nuclear magnetic resonance (NMR) measurements for (TMTTF)$_2$Br. The angular dependence of the AFMR fields at 1.5 K is different from that at 4.8 K, and the temperature dependence of the two AFMR modes is enhanced below 5 K. Furthermore, ^{2}D-NMR measurements were performed to investigate charge distribution by quadrupole splitting at low temperatures. We found that the ^{2}D-NMR spectrum changes at ~4 K in the antiferromagnetic phase. Successive phase transition and a possible magnetic structure are discussed.

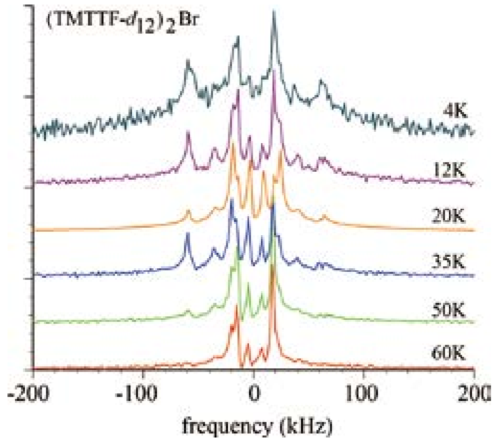

Figure 3. Temperature dependence of the ^{2}D-NMR spectra for deuterated (TMTTF)$_2$Br. Each spectrum is composed of several doublets because of quadrupole splitting.

References

1) S. Jin, M. Supur, M. Addicoat, K. Furukawa, L. Chen, T. Nakamura, S. Fukuzumi, S. Irle and D. Jiang, *J. Am. Chem. Soc.* **137**, 7817–7827(2015), and references therein.

2) T. E. Jin, M. Asada, Q. Xu, S. Dalapati, M. A. Addicoat, M. A. Brady, H. Xu, T. Nakamura, T. Heine, Q. Chen and D. Jiang, *Science* **357**, 673–676 (2017).

3) S. Kitou, T. Fujii, T. Kawamoto, N. Katayama, S. Maki, E. Nishibori, K. Sugimoto, M. Takata, T. Nakamura and H. Sawa, *Phys. Rev. Lett.* **119**, 065701 (2017).

Award

NAKAMURA, Toshikazu; The 22nd Outstanding Paper Award of the Physical Society of Japan (2017).