

Magnetic Resonance Studies for Functional Molecular-Based Solids

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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.

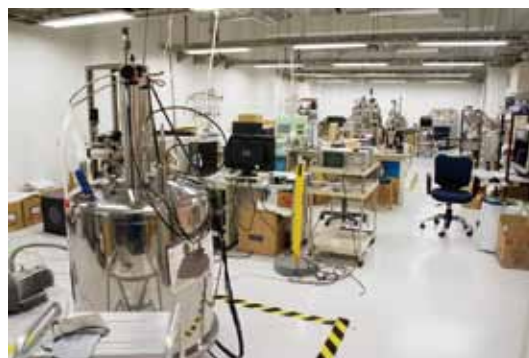


Figure 1. Solid state broad-line NMR system (above). Multi-frequency pulsed ESR system (below).

Selected Publications

- T. Terauchi, S. Sumi, Y. Kobayashi, T. Nakamura, K. Furukawa and Y. Misaki, "Stable Metallic State of $(\text{TTPCOO})_2\text{NH}_4$ with Mobile Dopant," *Chem. Commun.* **50**, 7111–7113 (2014).
- S. Jin, K. Furukawa, M. Addicoat, L. Chen, S. Takahashi, S. Irle, T. Nakamura and D. Jiang, "Large Pore Donor–Acceptor Covalent Organic Frameworks," *Chem. Sci.* **4**, 4505–4511 (2013).

1. Magnetic Resonance Investigation of Self-Doped Type TTF^{COO} and TTPCOO Family Salts

¹H-NMR and High-Field ESR measurements were carried out for self-doped type organic conductors, ammonium tetra-thiapentalene carboxylate (TTPCOO)₂[(NH₄⁺)_{1-x}(NH₃⁰)_x] (hereafter we abbreviated as TTPCOONH₄ system), which are developed by NIMS group. While the pristine TTPCOOH molecules are closed-shell, self-doped type carrier is generated by substitution of the end group of (NH₃⁰) with (NH₄⁺), which is regarded as a charge-reservoir. The π -extended system, TTPCOO, possessed a uni-axial g -tensor, indicating 2D isotropic structure such as herring-bone-like donor arrangements. NMR-relaxation rate shows the Korringa relation temperature dependence, and the ESR linewidth follows Elliot mechanism. These facts are apparent evidences of stable metallic state.

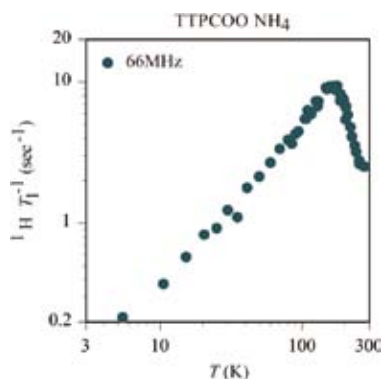


Figure 2. Temperature dependence of the ¹H-NMR spin-lattice relaxation rate T_1^{-1} for TTPCOO system. T -linear Korringa-like behavior down to 5 K indicates a stable metallic state.

Figure 2 shows the temperature dependence of the spin-lattice relaxation rate of TTPCOONH₄ system. A pronounced peak behavior observed at around 160 K shows frequency dependence and is apparently originated from the proton motion. Since the relaxation of molecular motion is rapidly suppressed as lowering temperature, the nuclear spin relaxation at low temperatures (*i.e.* below 100 K) is mainly caused by the electron spins. In the low-temperature region, the ¹H NMR spin-lattice relaxation rate, T_1^{-1} , of TTPCOONH₄ system shows T -linear Korringa-like behavior down to 5 K. This observation clarifies that this system is metallic. It is

contrast to the 1D spin diffusive relaxation behavior ($\sim T^{0.5}$) observed in a semiconductor (TTF^{COO})₂[(NH₄⁺)_{1-x}(NH₃⁰)_x]. The continuous T -linear behavior of T_1^{-1} down to 5 K also shows that there is no low-dimensional instability and anti-ferromagnetic (SDW) transitions at low temperatures. No obvious line shift and line broadening with temperature also supports this scenario. These facts indicate that substitution of mainframe from TTF to π extended TTP is essential key to realize a stable metallic state by means of reduction of electron correlation (Coulomb repulsion) and dispersion force.

2. Time-Resolved ESR Spectroscopy Investigation of Photoconduction Mechanism in Covalent Organic Framework (COF) Materials

Covalent organic framework (COF) materials are porous crystalline materials. They attracted much attention because of their functionalities. Recently, a variety of COF materials based on the Donor–Acceptor (D–A) system have been developed. Jiang and coworkers synthesized a variety of D–A type COFs such as NDI–ZnPc, PyDI–ZnPc and ZnPc–NDI–HHTP. While molecules are connected by tight covalent bonds within the two-dimensional layers, the molecules stack to form one-dimensional columns perpendicular to the planes. They show pronounced photo-conducting behavior. The possible photo-conduction origin is the electron transfer between donor and acceptor. However, the detail mechanism is an open question. We performed time-resolved photo-excited ESR spectroscopy for a series of D–A type COF materials to investigate the photo-conduction mechanism. After photo-excitation to D–A type COFs, an ESR signal originated from the charge-separated state was observed, which could not be observed in isolated molecules. As for ZnPc–NDI–COF, we can observe the charge-separated ESR signal even at R.T., indicating long lifetime of the photo-excited carriers. Actually, the lifetime of the photo-excited charge-separated states in ZnPc–NDI–COF are estimated as 865 μ s at 80 K and 1.8 μ s at 280 K.

References

- 1) K. Furukawa, T. Nakamura, Y. Kobayashi and T. Ogura, *J. Phys. Soc. Jpn.* **79**, 053701 (4 pages) (2010).
- 2) S. Jin, X. Ding, X. Feng, M. Supur, K. Furukawa, S. Takahashi, M. Addicoat, M. E. El-Khouly, T. Nakamura, S. Irle, S. Fukuzumi, A. Nagai and D. Jiang, *Angew. Chem., Int. Ed.* **52**, 2017–2021 (2013).