Magnetic Resonance Studies for Molecular-Based Conductors

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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 of these materials enables us to perform systematic investigations of low-dimensional, highly-correlated electron systems. Competition between the electronic phases in molecular-based conductors has attracted much attention. The investigations of such electronic phases by means of magnetic resonance measurements are important to understanding unsolved fundamental problems in the field of solid state physics.

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

1. Redistribution of Charge in the Proximity of the Spin-Peierls Transition: ¹³C NMR Investigation of (TMTTF)₂PF₆

Organic conductors, $(TMTTF)_2X$, have been extensively studied and are well-known quasi-one-dimensional conductors possessing various ground states, for example, spin-Peierls, antiferromagnetic, and superconductivity states realized by the application of pressure or variation of the counter-anion, $X^{(1)}$ However, recent progress in the investigation of chargeordering (CO) phenomena has cast doubts on the validity of the simple Mott-Hubbard insulator model. TMTTF-based salts show a resistivity minimum at T_{ρ} in the paramagnetic phase because of 1D electronic Umklapp processes. Below T_{ρ} , they are well described with a localized picture. At low-temperatures, most of them undergo charge-ordering transitions in the intermediate paramagnetic states between T_0 and the phasetransition temperature toward the ground state.²⁻⁴⁾ In our previous report,⁴⁾ the charge configuration patterns of the charge-ordering phases in the intermediate paramagnetic states, such as $-O-O-o-(2k_F)$ and $-O-o-O-o-(4k_F)$ along the stacking axes, were determined for several TMTTF salts

by ESR linewidth anisotropy analysis. We also clarified that the long-range Coulomb interaction along the stacking axis plays an essential role stabilizing the charge-ordering phases in the intermediate paramagnetic states.^{5–8)} However, the driving force and charge configuration of the ground state have not yet been clarified.



Figure 1. Temperature dependence of 13 C NMR spectra of (TMTTF)₂ PF₆. Measurements were performed at the so-called magic-angle configuration. The inset shows two inequivalent inner (solid large circles) and outer (small circles) 13 C sites in the zigzag TMTTF chains.

For example, the ground states of $(TMTTF)_2SbF_6$ (antiferromagnet) and $(TMTTF)_2AsF_6$ (spin-Peierls) are different from each other, although they possess the same charge configuration pattern in the intermediate paramagnetic phase. Moreover, the coexistence of two orders was established along with the existence of a tetracritical point in the temperature/ pressure phase diagram.⁹⁾ Hence, it is also an open question whether charge separation in the spin-Peierls phase of $(TMTTF)_2MF_6$ is likely or unlikely.

In this study, we performed pulsed 13 C NMR measurements on (TMTTF)₂PF₆ to determine its low-temperature electric states. (TMTTF)₂PF₆ shows a charge-ordering phase in the intermediate paramagnetic state below 65 K, and undergoes the spin-Peierls phase-transition at around 18 K. These

two successive phase-transition temperatures are the closest to each other among the family of TMTTF salts at ambient pressure. We present the electronic properties of this compound from a microscopic point of view.

2. Possible One-Dimensional Helical Conductor: Hexa-Peri-Hexabenzocoronene Nanotube

The discovery of electrically conductive carbon nanotube materials has expanded interest in exploring novel materials for functional electronic devices. Recently, new nanotubular objects have been developed by Aida and co-workers using novel hexa-peri-hexabenzocoronene (HBC) amphiphiles bearing hydrophilic oxyalkylene chains and lipophilic dodecyl chains. The amphiphilic HBC molecules have two lipophilic alkyl chains on one side, and two hydrophilic chains on the opposite side. Self-assembled graphitic nanotubes were obtained by cooling a hot tetrahydrofuran solution of the HBC derivative to room temperature. The HBC molecules stack to form well-defined nanotubes with a helical array of a large number of π -stacked HBC units.^{10–12)} In ordinary carbon nanotubes, the conjugated two-dimensional π -molecular wave functions are spread on the surfaces of the nanotubes. However, in the case of the HBC nanotubes, the π -conjugated columns stack in the direction of the one-dimensional chain. The HBC nanotubes possess a uniform diameter of 20 nm with a wall thickness of 3 nm. Since the HBC molecules have a closed-shell, the resistivity of the pristine HBC nanotube is very high (~MΩcm). By chemical oxidation using iodine, however, the HBC nanotubes show high electrical conductivity.13)

There have been remarkable recent developments in structural measurement techniques such as scanning electron microscopy (SEM) and X-ray crystallography. However, the HBC nanotubes are not crystalline and the iodine-doped phases are not stable in a vacuum: when placed in a vacuum, the iodine-doped HBC nanotubes return to reversibly to the form of pristine HBC nanotubes.¹³⁾ Hence, it is difficult to use such structural measurement techniques for the iodine-doped HBC nanotubes. Magnetic resonances measurements, on the other hand, are non-contact, low-energy spectroscopy techniques that are powerful even for non-crystalline materials. Moreover, with magnetic resonance investigations we can obtain not only static information but also dynamic details. In order to understand the origin and dynamics of charged carriers, in the present study, ESR and ¹H NMR measurements were carried out on the iodine-doped HBC nanotubes.

3. Anomalous Temperature Dependence of *g*-Tensor in Organic Conductor, $(TMTTF)_2X$ (X = Br, PF₆ and SbF₆)

The band-structures of organic conductors are deduced from frontier orbitals (for example, the highest occupied molecular orbital from a donor molecule) estimated by molecular orbital calculations applying the tight-binding approximation.¹⁾ The Fermi surfaces thus calculated are consistent with those estimated from quantum vibration and/or angular dependence magneto-resistance experiments.¹⁾ Most of the physical phenomena associated with organic conductors can be explained within a framework where the frontier orbital is treated as one rigid atomic orbital in an alkaline metal. It is commonly believed that the counter anions themselves do not affect the electronic properties of organic conductors.

An anomalous behavior of the *g*-tensor —a shift in principal value and rotation of the principal axes— was observed in $(TMTTF)_2X$ salts with decreasing temperature.^{14–16}) This behavior cannot be explained by a precursor effect (short-range magnetic fluctuation) just above the magnetic long-range order nor by molecular arrangement change.

In this study, we examined the magnetic properties for $(TMTTF)_2X$ (X = Br, PF_6 and SbF_6) with ESR spectroscopy, X-ray diffraction, and quantum-chemical calculation of the *g*-tensor. We attempted to explain the anomalous behavior of the *g*-tensor using a scenario where the symmetry of the frontier orbital is deformed by the external counter-anion potential. The intra-molecular spin-distribution as a function of temperature is discussed from the microscopic point of view.

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