

Magnetic Resonance Studies for Molecular-Based Conductors

Department of Materials Molecular Science
Division of Electronic Properties



NAKAMURA, Toshikazu
FURUKAWA, Ko
TAKAHASHI, Seiya
ABE, Hitomi

Associate Professor
Assistant Professor
Graduate Student*
Secretary

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.

1. ^{13}C NMR Study of the Magnetic Properties of the Quasi-One-Dimensional Conductor, $(\text{TMTTF})_2\text{SbF}_6$

Magnetic properties in the quasi-one-dimensional organic salt, $(\text{TMTTF})_2\text{SbF}_6$, where TMTTF is tetramethyltetrathiafulvalene, are investigated by ^{13}C NMR under pressures. Antiferromagnetic phase transition at ambient pressure (AFI) is confirmed. Charge ordering is suppressed by pressure and is not observed under 8 kbar. For $5 < P < 20$ kbar, a sharp spectrum and the rapid decrease of the spin-lattice relaxation rate $1/T_1$ were observed below about 4 K, which is attributed to a spin-gap transition. Above 20 kbar, an extremely broadened spectrum and a critical increase of $1/T_1$ were observed. This indicates that the system enters into another antiferromagnetic phase (AFII) under pressure. The slope of the antiferromagnetic phase transition temperature T_{AFII} , dT_{AFII}/dP , is positive, while T_{AFI} decreases with pressure. The magnetic moment is weakly incommensurate with the lattice at 30 kbar.

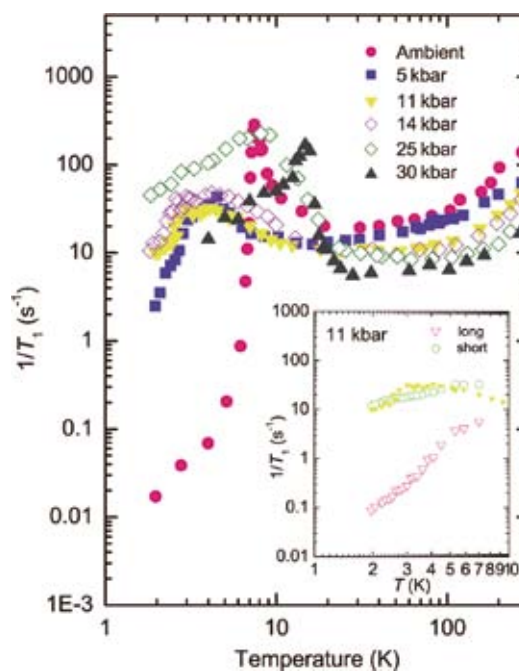


Figure 1. Temperature dependence of the ^{13}C -NMR spin-lattice relaxation rate, $1/T_1$, at six different pressures.

2. Time-Resolved ESR Study for Photoconductive Mechanism of Photoconductive TTF-Derivatives

The spin dynamics of photoconductive ethylene-dithiolotetrathiafulvalene (EDT-TTF) containing 1,3-benzothiazole (BTA) was examined for frozen solution and powdered samples using time-resolved electron spin resonance (TR-ESR) spectroscopy. While the TR-ESR signal of a frozen solution sample under visible excitation were attributed to the excited triplet state \mathbf{T}_1 , that of the powdered indicates a charge-separated state. It is a characteristic feature of molecular assembled system.

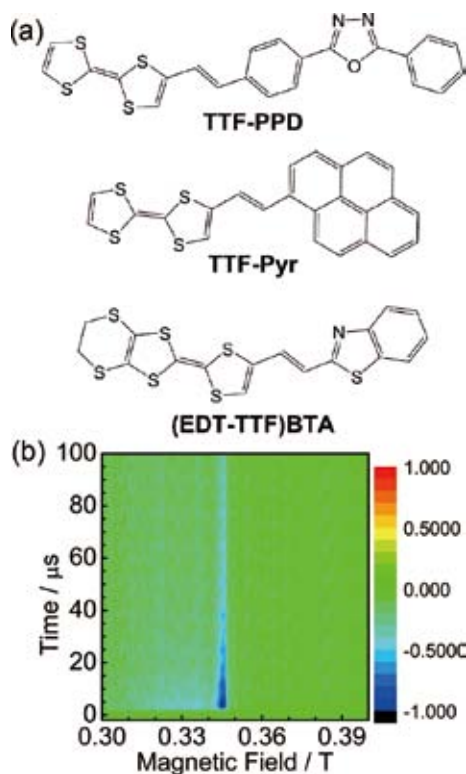


Figure 2. (a) Molecular structure of single-molecule-type photoconductive materials, TTF and EDT-TTF derivatives. (b) 2D pulsed TR-ESR spectra for powder sample of photoconductive EDT-TTF containing BTA. The normal axis represents the ESR signal intensity. The color scale denotes the signal intensity. Positive and negative values indicate the absorption and emission of microwaves, respectively.

3. Physical Properties of a Molecular Conductor (BEDT-TTF)₂I₃ Nanohybridized with Silica Nanoparticles by Dry Grinding

The dry grinding of a mixture of bis(ethylenedithio)tetra-thiafulvalene (BEDT-TTF) and silica nanoparticles has produced powdery (BEDT-TTF)–silica nanocomposites. The (BEDT-TTF)–silica nanocomposites are readily doped with iodine in hexane dispersion to give powdery nanocomposites of (BEDT-TTF)₂I₃–silica. XRD and TEM measurements suggest that (BEDT-TTF)₂I₃ in the nanocomposite exists as shell layers of core-shell-type nanoparticles and as nanometre-sized crystals incorporated into hollow sites of aggregated silica nanoparticles. Magnetic susceptibility measurements reveal that the nanocomposites accompanied a large number of Curie spins attributable to surface molecules of the core-shell-type nanoparticles. The nanocomposites show a magnetic susceptibility change corresponding to the metal–insulator transition of α -(BEDT-TTF)₂I₃ in a broad temperature range of 110–140 K, which is attributed to the properties of the nanocrystalline components. Doping in diethyl ether dispersion leads to higher amounts of the nanocrystalline component being obtained. The doping of (BEDT-TTF)–silica nanocomposites by dry

grinding produces a paramagnetic powder containing amorphous (BEDT-TTF)₂I₃, which possesses a Curie spin concentration of 50%. The effects of annealing on these nanocomposites are investigated. The electrical conductivity of the compaction pellets of (BEDT-TTF)–silica nanocomposites is enhanced by iodine doping to reach approximately 10^{-6} S cm⁻¹, but the value is much lower than that of the bulk crystals (10^1 S cm⁻¹).

4. Electronic Properties and ¹H Dynamics in Self-Doped Organic Conductor (TTF₂COO)[(NH₄⁺)_{1-x}(NH₃)_x]

¹H-NMR and High-Field ESR measurements were carried out for self-doped type organic conductor, (TTF₂COO)[(NH₄⁺)_{1-x}(NH₃)_x] and its deuterated salt. (TTF₂COO)[(NH₄⁺)_{1-x}(NH₃)_x] and related salts are TTF-based self-doped hydrogen-bonding conductor developed by NIMS group. The TTF-skeleton stacks to form a one-dimensional column. The pristine TTF₂COONH₄ molecule is 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. Actually, a considerable concentration of NH₃ molecules has been confirmed by X-ray photoelectron spectroscopy data. According to the static magnetic susceptibility and high-field ESR measurements, we found that the observed spin was distributed on quasi-hole-like TTF skeletons, and that the TTF₂COO mainframe partially becomes a neutral radical. The spin susceptibility was well fitted with a Curie-Weiss term and an activation-type term. The activation-type term was dominant at high temperatures.

In order to clarify the ¹H dynamics, we carried out ¹H-NMR measurements for pristine and deuterated salts. The ¹H-NMR spin-lattice relaxation rate, ¹H- T_1^{-1} , of indicates a characteristic temperature and frequency dependence. A pronounced peak observed at around 200 K is possibly due to molecular motion. Since the relaxation curve is not single component below 200 K, we assumed the ¹H- T_1^{-1} from initial slope (weighted average). Below 100 K ¹H- T_1^{-1} follows $T^{0.5}$, and remains frequency dependence, indicating a 1D spin-diffusion type relaxation. However, the Fermi surface of (TTF₂COO)[(NH₄⁺)_{1-x}(NH₃)_x] is considered to be 2D, according to the tight-binding band calculation. This discrepancy is an open question at present.

References

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* carrying out graduate research on Cooperative Education Program of IMS with Yokohama National University