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 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. Structural Investigation of the Spin-Singlet Phase in $(TMTTF)_2I$

To elucidate the electronic state that exists in the boundary region between the spin-singlet phase and the high-pressure side antiferromagnetic phase in the modified generalized phase diagram, we carried out x-ray diffraction, electron spin resonance, and nuclear magnetic resonance measurements of the tetramethyl-tetrathiafulvalene (TMTTF) family salt, $(TMTTF)_2I$. The unit-cell volume of $(TMTTF)_2I$ is between that of $(TMTTF)_2Br$ and $(TMTTF)_2PF_6$. We found that $(TMTTF)_2I$ undergoes a spin-singlet phase transition at 21 K without involving paramagnetic charge-ordering phase. Therefore, the charge-ordering transition is not necessary for the spin-singlet transition of TMTTF salts as seen in other conventional spin-singlet salts. Finally, we discuss possible mechanisms of the spin-singlet phase transition.

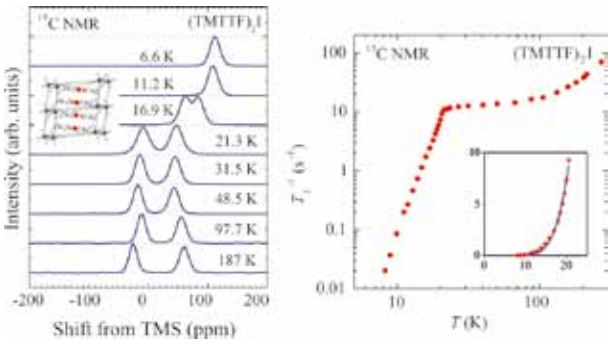

Figure 1. (Left) Temperature dependence of the ^{13}C-NMR spectra of a single crystal of $(TMTTF)_2I$ Frequencies are referenced against tetramethylsilane. (Right) Temperature dependence of the ^{13}C-NMR, spin-lattice relaxation rate, T_1^{-1}, of $(TMTTF)_2I$. The inset is the low-temperature region, drawn with a linear scale. The blue line shows fitting results that assumed a simple gap, with $\Delta \sim 128$ K.

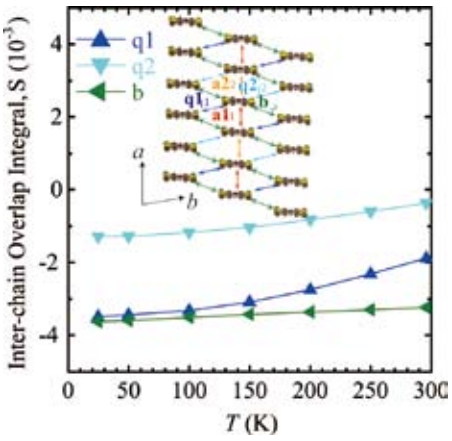

Figure 2. Temperature dependence of the overlap integral of $(TMTTF)_2I$ down to 25 K focusing on the inter-chain overlap integral. The overlap parameters within the *ab*-plane are defined in the inset.

2. Photoinduced Triplet States of Photoconductive TTF Derivatives Including a Fluorescent Group

The spin dynamics of photoconductive tetrathiafulvalene (TTF) derivatives containing 2,5-diphenyl-1,3,4-oxadiazole (PPD) was examined using time-resolved electron spin resonance (TR-ESR) spectroscopy. TR-ESR signals of a frozen solution sample under visible excitation were attributed to the excited triplet state $\mathbf{T}_1$, which was populated via intersystem crossing from the excited singlet state $\mathbf{S}_1$ as confirmed by TR-ESR spectral simulations. From DFT calculations, the spin density distribution of the $\mathbf{T}_1$ state was found to be concentrated around the linker between the TTF and PPD molecules.

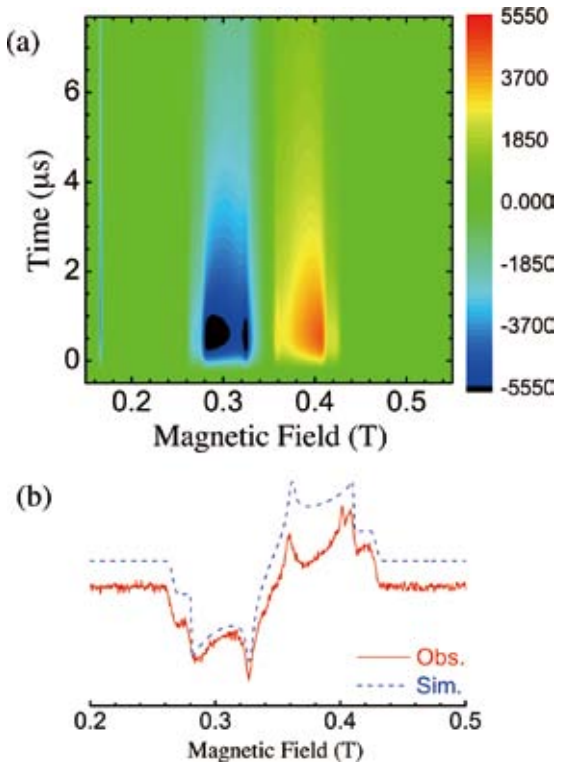

Figure 3. (a) 2D pulsed TR-ESR spectra for photoconductive TTF derivatives containing PPD. The normal axis represents the ESR signal intensity. The color scale denotes the signal intensity. Positive and negative values indicate the absorption and emission of microwaves, respectively. (b) Slice spectra along the magnetic field axis at t = 0.5 μs and T = 20 K. The solid and dotted lines denote the observed and simulated spectra, respectively.

3. Magnetic Memory Based on Magnetic Alignment of a Paramagnetic Ionic Liquid near Room Temperature

A paramagnetic ferrocenium-based ionic liquid that exhibits a magnetic memory effect coupled with a liquid–solid phase transformation has been developed. Based on field alignment of the magnetically anisotropic ferrocenium cation, the magnetic susceptibility in the solid state can be tuned by the weak magnetic fields (< 1 T) of permanent magnets.

4. Completely Hydrostatic Pressure Effect of Anisotropic Resistivity in the 1-D Organic Conductor $(TMTTF)_2SbF_6$

The anisotropic resistivity of $(TMTTF)_2SbF_6$ under hydrostatic pressure was investigated up to ~0.3 GPa using a helium gas pressure control system. The resistivity along the a axis shows a metallic behavior above a crossover temperature T_ρ (~220 K at ambient pressure) and an insulating behavior below T_ρ. On the other hand, the temperature dependence of ρ_b, and ρ_c was found to show a kink at a charge ordered temperature T_{CO}. Interestingly, T_ρ was increased with applying pressure while T_{CO} was decreased with applying pressure. We discuss this unusual feature in terms of the pressure–temperature phase diagram in the $(TMTCF)_2X$ system.

5. ^{13}C NMR Study of the Magnetic Properties of the Quasi-One-Dimensional Conductor, $(TMTTF)_2SbF_6$

Magnetic properties in the quasi-one-dimensional organic salt $(TMTTF)_2SbF_6$ are investigated by ^{13}C 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, attributed to a spin-gap transition. However, as the reduction of the Knight shift was not observed, the phase is not conventional non-magnetic spin-Peierls. Above 20 kbar, extremely broadened spectrum and 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.

References

1) K. Furukawa, K. Sugiura, F. Iwase and T. Nakamura, *Phys. Rev. B* **83**, 184419 (5 pages) (2011).
2) K. Furukawa, Y. Sugishima, H. Fujiwara and T. Nakamura, *Chem. Lett.* **40**, 292–294 (2011).
3) Y. Funasako, T. Mochida, T. Inagaki, T. Sakurai, H. Ohta, K. Furukawa and T. Nakamura, *Chem. Commun.* **47**, 4475–4477 (2011).
4) M. Itoi, Y. Ishii, H. Kitano, S. Takekoshi, K. Matsubayashi, Y. Uwatoko and T. Nakamura, *Physica C* **470**, S594–S595 (2011).