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.

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

Covalent organic framework (COF) materials are porus 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 μs at 80 K and 1.8 μs at 280 K.

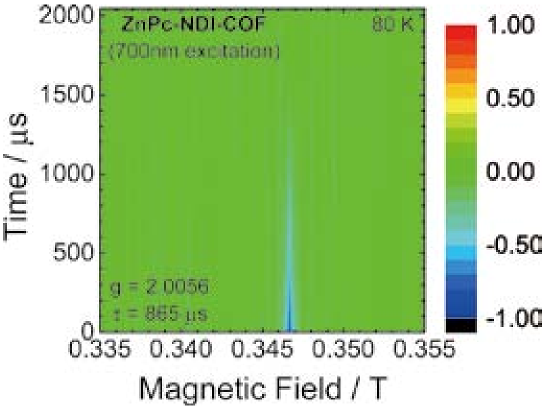

Figure 1. 2D pulsed TR-ESR spectra for ZnPc-NDI-COF. The normal axis represents the ESR signal intensity. The color scale denotes the signal intensity. Positive and negative values indicate the absorption and emission of microwaves, respectively.

2. Simultaneous Control of Carriers and Localized Spins with Light in Organic Materials

Photoconduction and its related phenomena have been known for quite some time, and have attracted a significant amount of scientific attention. Photoconduction is applied in devices, sensors, detectors, and energy converters, such as charge-coupled devices, complementary metal oxide-semiconductor image sensors, and photovoltaic cells, in addition to other advanced applications under investigation. In all known photoconductors, photoexcitation (PE) controls only the carriers. Herein, a new photoconductor is reported, in which the carriers and localized spins can be simultaneously controlled with UV irradiation. This material transforms from a semiconductor to a metal under irradiation, distinguishing it from all existing photoconductors. Furthermore, an interaction between the carriers and localized spins has been discovered, which enables the localized spins to be controlled and detected by the carriers and vice versa. In addition, the photoconduction is unique because it exhibits wavelength selectivity. The selectivity means that the photoconduction mechanism is different from currently known mechanism. No material has been found in which the carriers and localized spins can be simultaneously generated with light. If the carriers and localized spins are controlled using light (i.e., via PE), it may be possible to enhance this control over a wider range, beyond the restrictions of thermodynamic equilibrium. In order to find such a material, a promising starting point is to investigate charge-transfer salts consisting of a photochemical redox pair, because, under irradiation, the redox reaction transfers a larger number of electrons between pairs, and thus produces, by far, a larger number of carriers and localized spins than using PE alone. Following a series of examinations of a variety of charge-transfer salts, focus was placed on salts of $[Ni(dmit)_2]_n^-$ (dmit = 1,3-dithiol-2-thione-4,5-dithiolate; $0 \leq n \leq 2$) and methyl viologen (MV_n^+). $Ni(dmit)_2$ molecules are known to form conducting solids with multiredox properties, while the MV is expected to be a spin source under irradiation because of its characteristic photochemical redox reactivity. Herein, a strategy for realizing photomagneticconductors is proposed and demonstrated based on the electrical and magnetic properties of $MV[Ni(dmit)_2]_2$.

3. Organometallic Ionic Liquids from Alkyloctamethylferrocenium Cations: Thermal Properties, Crystal Structures, and Magnetic Properties

Alkyloctamethylferrocenium salts with the Tf_2N anion ($[Fe(C_5Me_4C_nH_{2n+1})(C_5Me_4H)][Tf_2N]$; Tf_2N = bis-(trifluoromethanesulfonyl)amide) were prepared, and their ionic liquid properties, thermal properties, crystal structures, and magnetic properties were investigated. The melting points of the Tf_2N salts were near room temperature, and decreased with increasing alkyl chain length up to $n = 8$ and then increased.

The salts with PF_6 and NO_3 anions were also prepared. The melting points of the PF_6 salts were higher than 100 °C. Most of these salts exhibited phase transitions in the solid state. The sum of the entropies of the melting and solid phase transitions was nearly independent of the alkyl chain length for salts with short alkyl chains, whereas those for salts with longer alkyl chains ($n \geq 10$ for Tf_2N salts, $n \geq 6$ for PF_6 salts) increased with increasing alkyl chain length. Crystal structure determinations revealed that the short chain salts form simple alternately packed structures of cations and anions in the solid state, and that the long chain salts form lamellar structures, in which the alkyl chains are aligned parallel between the layers. The effects of magnetic fields on the crystallization of the paramagnetic ionic liquids were investigated, and revealed that the Tf_2N salts with $n = 4$ exhibited magnetic orientation when solidified under magnetic fields. The magnetic orientation was shown to be a bulk phenomenon, and the importance of the magnetic anisotropy of the crystal structure was suggested in comparison with the response of other Tf_2N salts.

4. Magnetic Resonance Investigation of Self-Doped Type TTFCOO and TTPCOO Family Salts

^{1}H-NMR and High-Field ESR measurements were carried out for self-doped type organic conductor, TTFCOO and TTPCOO derivatives. We found the conducting electrons both for TTFCOO and TTPCOO derivatives. But the spin susceptibility shows significant activation-type contribution and the ^{1}H-NMR spin-lattice relaxation rate, $^1\text{H-}T_1^{-1}$, shows a 1D electron spin-diffusion type relaxation for TTFCOO derivative. On the other hand, TTPCOO derivative shows metallic behavior down to the lowest temperatures. Detailed comparison between TTFCOO and TTPCOO salts is investigated.

References

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Award

FURUKAWA, Ko; SEST Young Investigator Award (2012).

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