

# 博士論文（要約）

## NMR Study of Electronic States in the Multi-Orbital Organic Conductor $M(\text{tmdt})_2$

（多軌道系有機導体  $M(\text{tmdt})_2$  の電子状態に関する NMR 研究）

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In this thesis, we studied the electronic states in a series of isostructural organic conductors  $[M(\text{tmdt})_2]$  ( $M = \text{Pt}, \text{Ni}, \text{Au}$  and  $\text{Cu}$ ) through  $^1\text{H}$  and  $^{13}\text{C}$  NMR experiments. The family of  $[M(\text{tmdt})_2]$ , which is known to show a variety of physical properties depending on  $M$ , are exceptional organic conductors that possess the orbital degrees of freedom. The degeneracy is varied by replacing  $M$  with keeping the crystal symmetry and molecular structure. Another uniqueness of  $[M(\text{tmdt})_2]$  is large compressibility, which enables us to vary the electron correlation by relatively low hydrostatic pressure. These features and diverse physical properties provide an opportunity to understand the electron correlation in multi-orbital systems in a systematic way. In the present experimental work, we sought for a united view of the electronic states in the isostructural  $[M(\text{tmdt})_2]$  ( $M = \text{Pt}, \text{Ni}, \text{Au}$  and  $\text{Cu}$ ) in the light of the electron correlation and the orbital degeneracy, and also explored the novel physical properties under pressure.

We first investigated how the electronic states changed by *the replacement of M*. To know the orbital states responsible for magnetism, we performed  $^{13}\text{C}$  and  $^1\text{H}$  nuclear magnetic resonance (NMR) measurements for this family at ambient pressure. The  $^{13}\text{C}$  spectra were found strongly  $M$ -dependent, which revealed that the orbital states were not the same among  $[M(\text{tmdt})_2]$ . The results for compounds other than  $M = \text{Au}$  were almost consistent with the picture that  $M = \text{Pt}$  and  $\text{Ni}$  salts were the  $L\pi$  orbital systems, while  $M = \text{Cu}$  salt was a hybrid system of the  $dp\sigma$  and  $L\pi$  orbitals. From the detailed analyses of the obtained spectra, it was found that  $M = \text{Au}$  salt was a hybrid system with the  $dp\sigma$  and  $L\pi$  orbitals both contributing to the magnetism.

Then, we proceeded to investigate the electronic states of  $[M(\text{tmdt})_2]$  *at ambient pressure*. For  $M = \text{Pt}$  and  $\text{Ni}$  salts,  $^{13}\text{C}$  NMR data of relaxation rate and Knight shift revealed the paramagnetic metallic behavior, consistent with the preceding experiments, and also suggested the existence of extraordinarily slow dynamics persistent at least down to 2 K. It should be pointed out that the characteristics of the dynamics are quite distinct from the widely observed local motion of alkyl or alkylene groups on the edges of the molecules, indicating the unique molecular dynamics in  $[M(\text{tmdt})_2]$ . We proposed that the molecular deformational degrees of

freedom inherent to the  $M(\text{tmdt})_2$  molecule such as a twisting motion of tmdt ligands might be responsible for the anomalous dynamics.

For  $M = \text{Cu}$  and  $\text{Au}$  salts, we observed the antiferromagnetic (AF) transitions in both compounds. The characteristics of the AF transition such as transition temperature and AF moment were contrasting between the two compounds. For  $M = \text{Cu}$  salt, the comparison of  $^{13}\text{C}$  and  $^1\text{H}$  relaxation rates revealed the spin dynamics of the  $dp\sigma$  and  $L\pi$  orbitals respectively, and  $[\text{Cu}(\text{tmdt})_2]$  is concluded to be a hybrid of the  $dp\sigma$ -orbital AF Mott insulator and the  $L\pi$ -orbital band insulator due to strong dimerization. For  $M = \text{Au}$  salt, the analysis of the  $^{13}\text{C}$  spectra in the AF phase showed that the AF moment was located substantially on the  $L\pi$  orbitals. Considering the experimental results and the  $L\pi$ - $dp\sigma$  multi-orbital nature, we proposed two models for the ground state of  $[\text{Au}(\text{tmdt})_2]$ , depending whether the AF moment was carried by the  $L\pi$  orbital or the  $dp\sigma$  orbital.

These results and discussion suggested that the replacement of  $M$  does change the orbital degeneracy, thus resulting in a variety of electronic states in  $[M(\text{tmdt})_2]$ .

Next, we performed  $^1\text{H}$  and  $^{13}\text{C}$  NMR measurements for  $M = \text{Pt}$ ,  $\text{Au}$ , and  $\text{Cu}$  compounds *under hydrostatic pressures*. We succeeded in obtaining  $^{13}\text{C}$  NMR signal with good signal-to-noise ratio under pressure by utilizing water as a pressure medium instead of conventionally used oil, which caused spurious  $^{13}\text{C}$  signal harmful to experiments. The  $^{13}\text{C}$  NMR study on  $M = \text{Pt}$  salts showed a decrease of  $(^{13}T_1T)^{-1}$  by pressure, indicating the increase in the band-widths with pressure. It was also found that the anomalous slow dynamics was suppressed under pressures. The  $^1\text{H}$  NMR study on  $M = \text{Au}$  and  $\text{Cu}$  salts showed sudden disappearances of the AF transitions at a critical pressure, where the relaxation rate suddenly changed both in magnitude and temperature dependence. Taking account of the abrupt change and the similarity to the pressure dependence in  $M = \text{Au}$  and  $\text{Cu}$  salts, we proposed a Mott transition on the  $dp\sigma$  orbital for both compounds. Assuming their different degree of the  $L\pi$ - $dp\sigma$  orbital degeneracy, we also considered a possible valence transition in  $[\text{Au}(\text{tmdt})_2]$  and the Mott transition in  $[\text{Cu}(\text{tmdt})_2]$ . In both scenarios, the concomitant enhancement of the molecular dynamics is expected to be triggered by the change in the electronic states of  $dp\sigma$  orbital. Across the band-selective Mott transition or the valence transition, the electron population in the relevant orbital can change because of possible electron transfer between different orbitals and

the valence of  $M = \text{Au}$  and  $\text{Cu}$  could fluctuate. The interplay between the electron correlation and orbital hybridization may give rise to a new kind of instability in the molecular structure, whose conformation is quite sensitive to the electron occupation in the  $d_{xy}$  orbital, resulting in inducing or enhancing the twisting motion of tmdt ligand under pressures. This scenario may explain why the change of the whole temperature-profile of the relaxation rate occurred coincidentally with the disappearances of the AF transitions in  $M = \text{Au}$  and  $\text{Cu}$  salts. The present work suggests that the electron correlation, orbital degrees of freedom, and molecular dynamics are intimately coupled and their interplay is a key to comprehend the various physical properties in  $[\text{M}(\text{tmdt})_2]$ .

The softness of organic conductors allows a wide variation of parameters such as electron correlation, lattice geometry and so on, and has made significant contributions to elucidating physics behind the emergence in condensed matter. In this thesis, we have investigated the electronic states in the strongly-correlated multi-orbital organic conductors in the light of electron correlation and orbital degeneracy. On top of that and unexpectedly, the molecular dynamics and electronic states are found to be affected by each other. The potential interaction between the electron degrees of freedom and the molecular-structure degree of freedom is a unique outcome of the soft molecular material. We believe that developing such novel cooperation between multiple degrees of freedom will extend the frontier of the emergent phenomena in condensed matters.