Condensed Molecular Materials Laboratory
Chief Scientist: Reizo Kato (D.Sci.)

(0) Research field

CPR Subcommittee**:** Physics, Chemistry
Keywords: Molecular conductors, Strongly correlated electron system, Metal complexes, Field effect transistor (FET)

(1) Long-term goal of laboratory and research background

Synthesis, characterization and design of molecular materials, especially molecular metals (superconductors), have been undertaken. Molecular conductors exhibit a variety of physical properties which can be systematically understood on the basis of "simple" and "clear" electronic structures. From a chemical point of view, the most fascinating character of the molecular conductor is its "designability", that is, we can finely control solid state properties with chemical modifications of the molecule. The newly synthesized materials are characterized by the X-ray diffraction method and physical measurements (electrical conductivity, etc.). The electronic structure is investigated by the simple band structure calculation. All these results are devoted to the design of new molecular materials.

(2) Current research activities (FY2019) and plan (until Mar. 2025)

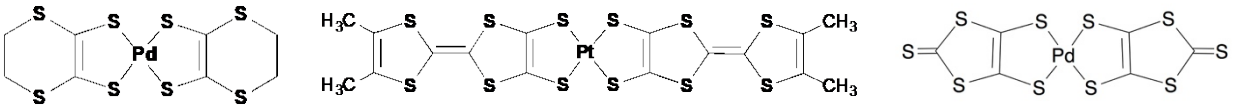
(a) Dirac electron system derived from HOMO-LUMO interactions in single-component molecular conductor

Molecular conductors are thought to have simple and clear electronic structures where the tight-binding approximation can be commonly applied. In conventional molecular conductors, each molecule provides one kind of frontier molecular orbital (HOMO or LUMO) that determines electronic properties. In recent years, however, it has been reported that an increasing number of molecular conductors cannot be categorized to such a single-orbital system. This means that we should expand our perception toward a multi-orbital system where more than two molecular orbitals in the same molecule contribute to electronic properties and the orbital degree of freedom plays an essential role.

Metal dithiolene complexes with a planar central core are characterized by a small HOMO-LUMO energy gap, and thus can provide a variety of multi-orbital molecular conductors. We found that the overlap of HOMO and LUMO bands leads to the emergence of Dirac points around the Fermi level in a single-component molecular crystal [Pd(dddt)$_2$] (Fig. 1) under high pressure generated by DAC (Diamond Anvil Cell).

We performed single crystal synchrotron X-ray diffraction measurements for [Pd(dddt)$_2$] under high pressure where the system is expected to turn into a Dirac electron system from a band insulator. The crystal that consists of two crystallographically independent [Pd(dddt)$_2$] molecules on the inversion centers retains the space group of $P2_1/n$ up to 8 GPa. A tight-binding model based on the crystal structure at 6 GPa indicates that the system is a nodal line semimetal where the Dirac point describes a loop within the first Brillouin zone. The Dirac cone in this system is associated with the crossing of the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) bands that originate from different molecular layers. The Dirac point emerges when the HOMO and LUMO bands meet on the surface where HOMO-LUMO couplings are absent. The deviation of the band energy at the Dirac point from the Fermi level is very small. Theoretical analyses indicate that the topological number is 1 and thus the system is a strong three-dimensional topological semimetal where all surfaces have surface states.

These results indicate that single-component molecular conductors can easily provide such a type of Dirac electron system. We demonstrated that a single-component molecular conductor [Pt(dmdt)$_2$] (Fig. 1) reported by Zhou et al. exhibits a typical and simple example of the Dirac cone formation mechanism in the single-component molecular conductors. (Research achievements 1, 5)



Pd(dddt)$_2$ Pt(dmdt)$_2$] Pd(dmit)$_2$

Fig. 1 Component molecules of molecular conductors

(b) A Discrepancy in Thermal Conductivity Measurement Data of Quantum Spin Liquid $EtMe_3Sb[Pd(dmit)_2]_2$

Quantum spin liquid (QSL) proposed by P. W. Anderson in 1973 exhibits the absence of magnetic or valence bond solid order among entangled quantum spins even at zero temperature. Although this third fundamental state for magnetism is a long-sought state of matter that has attracted much theoretical attention, the ground state and low-energy excitations of the S=1/2 antiferromagnetic triangular lattice are still far from full understanding and furthermore there are few candidates of real materials. In a series of anion radical salts of a metal complex $Pd(dmit)_2$ (Fig. 1), we found a promising candidate for QSL, $EtMe_3Sb[Pd(dmit)_2]_2$.

In 2010, the Kyoto Univ. group reported high thermal conductivity (κ) with the gapless behavior, which gave a strong impact on the study of the ground state of QSL. Recently, however, two groups (Sherbrooke Univ. and Fudan Univ.) claimed that the thermal conductivity is much smaller than the previous data and the gapless behavior cannot be observed. After these reports, it was suggested that this disagreement of the thermal conductivity data possibly originates from an existence of two types of crystals, the high κ crystal and the low κ crystal. An origin of the low κ data is thought to be micro cracks or the domain formation associated with the cation disorder. We checked crystals used for the κ measurements at Kyoto Univ. and Sherbrooke Univ. and pristine crystals using the X-ray diffraction method. The X-ray diffraction measurements revealed that all samples have a high crystalline quality and there is no significant difference between the high κ samples and the low κ samples. There is no aged deterioration. In addition, SEM characterization of Sherbrooke samples did not indicate the presence of any micro-cracks. In conclusion, we could find no problem in the samples at present (that is, there are NOT two types of crystals), and the method of measurements should be reconsidered. (Research achievements 2, 5)

(3) Members as of March, 2020

(Chief Scientist)
Reizo Kato

(Senior research scientist)
Shigeki Fujiyama, Yugo Oshima, Masae Horinouchi

(Research scientist)
Hengbo Cui

(Postdoctral researcher)
Takaaki Minamidate, Masashi Uebe

(Assistant)
Yumi Kuramitsu

(4) Representative research achievements

1. "A Tight-binding Model of an Ambient-pressure Molecular Dirac Electron System with Open Nodal Lines", R. Kato, and Y. Suzumura, J. Phys. Soc. Jpn. **89**, 044713/1-5 (2020).
2. "Thermal Conductivity of the Quantum Spin Liquid Candidate $EtMe_3Sb[Pd(dmit)_2]_2$: No Evidence of Mobile Gapless ", P. Bourgeois-Hope, F. Laliberte, E. Lefrancois, G. Grissonnanche, S. Rene de Cotret, R. Gordon, S. Kitou, H. Sawa, H. Cui, R. Kato, L. Taillefer, and N. Doiron-Leyraud, Phys. Rev. X, **9**, 041051/1-8 (2019).
3. "Two-dimensional ground-state mapping of a Mott-Hubbard system in a flexible field-effect device ", Y. Kawasugi, K. Seki, S. Tajima, J. Pu, T. Takenobu, S. Yunoki, H.M. Yamamoto, and R. Kato, Science Advances, **5**, eaav7282/1-9 (2019).
4. "Fragmented Electronic Spins with Quantum Fluctuations in Organic Mott Insulators Near a Quantum Spin Liquid", S. Fujiyama and R. Kato, Phys. Rev. Lett., **122**, 147204/1-6 (2019).
5. "Multi-Orbital Molecular Conductors Based on Metal Dithiolene Complexes", R. Kato, ISCOM2019 (The 13th International Symposium on Crystalline Organic Metals, Superconductors and Magnets), Tomar, Portugal (September, 2019).

Laboratory Homepage

https://www.riken.jp/en/research/labs/chief/condens_mol_mater/index.html
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