Intramolecular Fragmentation of Magnetic Moments by Multi-Orbital Effect in $X[Pd(dmit)_{2}]_2$ Near Quantum Spin Liquid

S. Fujiyama, R. Kato

RIKEN, Condensed Molecular Materials Laboratory, Wako 351-0198, Japan, e-mail: fujiyama@riken.jp

$X[Pd(dmit)_{2}]_2$ ($X^+ =$ onium cation) is known to exhibit a quantum spin liquid (QSL) state ($X =$ EtMe$_3$Sb) adjacent to antiferromagnetic (AF) long range orders. The proposed QSL-AF phase diagram parametrized by the anisotropy of the transfer integrals of the triangular network is consistent with single band dimer-Mott models [1], by which the electronic structure of Pd(dmit)$_2$ salts is considered to consist of the half-filled HOMO band.

We performed $^{13}$C NMR for $X =$ Me$_4$P ($T_N = 40K$) and Me$_4$Sb ($T_N = 12K$). The spectra and nuclear spin-lattice relaxation rates ($1/T_1$) above $T_N$ confirm nearly the same hyperfine constants and spin densities of $2p_z$ orbital for four independent $^{13}$C sites. However, in the antiferromagnetic state, the spectra show unconventional distinct peaks as shown in Fig. 1(b), which requires two kinds of ordered moments. The ratio of the magnitudes of the moments exceeds 2, which cannot be reproduced by simple magnetic models for $S = 1/2$. The x-ray diffraction study shows the inversion center in each [Pd(dmit)$_2$]$_2$ dimer is conserved even across $T_N$, and as a result, we determined the magnetic structure of $X[Pd(dmit)_{2}]_2$ ($X =$ Me$_4$P, Me$_4$Sb) as shown in Fig. 1(a) [2]. Here, the ordered moments are fragmented in each Pd(dmit)$_2$ molecule, which sheds light on the electronic structure of each molecule.

Contrasting to TTF-based organic conductors, the energy gap between the HOMO and LUMO for Pd(dmit)$_2$ is as small as 0.8 eV that is 1/3 of those of TTF derivatives due to the absence of $\pi$-d bond in HOMO. We consider the hybridization of HOMO and LUMO causes the significant imbalance of the spin densities across the central Pd ion, which was also suggested by recent RPA calculation [3]. This work claims the HOMO-LUMO hybridization in metal complexes works as a new degree of freedom to the magnetism, which can stabilize unconventional electronic states including quantum liquids.

Fig. 1. (a) Magnetic structure of Me$_4$P[Pd(dmit)$_2$]$_2$. The ‘i’ indicates the intradimer inversion center. (b) Antiferromagnetic $^{13}$C NMR spectra of a Me$_4$P[Pd(dmit)$_2$]$_2$ single crystal. Green and yellow hatches correspond to the magnetic moments in Fig. 1(a).

References