

Thermodynamic Studies of Novel Molecular Ferromagnets in Dimer-Mott Charge Transfer Compounds

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We report systematic experimental results of low-temperature heat capacity measurements of multi-layer dimer-Mott molecular compounds especially focusing on $X[\text{Ni}(\text{dmit})_2]_2$ ($X = \text{ethyl-4-bromothiazolium (Et-4BrT)}$, $\text{ethyl-2-iodo-5-bromopyridinium (Et-2I-5BrP)}$, and $\text{ethyl-2-iodo-5-bromopyridinium (Et-2,5-DBrP)}$), where dmit is 1,3-dithiole-2-thione-4,5-dithiolate. Since the valence of counter cations X is monovalent, $\text{Ni}(\text{dmit})_2$ dimer which form two dimensional β -analogous lattices give originally half-filled electronic states. These compounds are similar structure with typical organic charge transfer complexes which shows superconductivity, spin liquid, and charge glass phenomena. When the band width W is not so large as compared with the site coulomb repulsion U , the system shows Mott insulating features according to the scenario of Mott-Hubbard physics. [1-3] The peculiar structural feature of these series compounds is that the counter cations of X are stacked in the same direction and have net polarization which affect slightly on the electronic filling of the π -electrons layers. The order of the magnitude of net polarization was evaluated as $\text{Et-4BrT} > \text{Et-2I-5BrP} > \text{Et-2,5-DBrP}$.

The systematic heat capacity measurements using single crystal samples of $(\text{Et-4BrT})[\text{Ni}(\text{dmit})_2]_2$, $(\text{Et-2I-5BrP})[\text{Ni}(\text{dmit})_2]_2$ and $(\text{Et-2,5-DBrP})[\text{Ni}(\text{dmit})_2]_2$ were performed by the relaxation calorimetry technique. We succeeded to detect a peak in association with long-range ordering of π -electron spins around 1 K with large transition entropy of about 40-50% of $R \ln 2$ in these three compounds, suggesting that long-range ordering occurs. We also observed an upward shift of the peak structure when the magnetic fields is applied perpendicular to the layers in $(\text{Et-4BrT})[\text{Ni}(\text{dmit})_2]_2$, which indicates that the ferromagnetic behavior occurs as a bulk feature. The susceptibility measurement also shows the feature of bulk ferromagnet with ordered moment of $0.5 \mu_B$. In contrast to $(\text{Et-4BrT})[\text{Ni}(\text{dmit})_2]_2$, $(\text{Et-2I-5BrP})[\text{Ni}(\text{dmit})_2]_2$ and $(\text{Et-2,5-DBrP})[\text{Ni}(\text{dmit})_2]_2$ showed small magnetic field dependence which indicates paramagnetic like and anti-ferromagnetic behavior, respectively. The systematic difference observed in the thermodynamic features under magnetic fields can be interpreted as a kind of doping through the net polarization of counter cations may induce ferromagnetic interactions in the π -electrons layer. The antiferromagnetic grand state due to electron correlations in the dimer-Mott layer has been converted to a bulk ferromagnetic state through doping of slight amount of hole carriers.

It will be also discussed that the further doping using large dipolar cations can lead the system into a metallic state. As a matter of fact, the low temperature heat capacity of $(\text{Me-3,5-DIP})[\text{Ni}(\text{dmit})_2]_2$ shows linear $C_p T^{-1}$ vs T^2 at low temperature with finite electronic heat capacity coefficient γ . [3] The application of external pressure up to 1.0 GPa leads the ferromagnetic ground state to a kind of enhanced metallic state also in the case of $(\text{Et-4BrT})[\text{Ni}(\text{dmit})_2]_2$. The external pressure and doping can change this ferromagnetic ground state to metallic ones with strong ferromagnetic fluctuations. The relation with the metallic states realized in these multi-layer compounds is also discussed from thermodynamic viewpoints.

[1] T. Kusamoto *et al. Inorg. Chem.*, 52(9), 4759–4761 (2013).

[2] T. Kusamoto *et al. Inorg. Chem.*, 51(21), 11645–11654 (2012).

[3] Y. Kosaka *et al. J. Am. Chem. Soc.*, 129(11), 3054–3055 (2007).