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Study of the magnetic properties of variable spin network formed by organic radical crystals

Abstract

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Organic radicals consisting only of light elements have negligibly small spin-orbit coupling and therefore behave as ideal Heisenberg spin systems bearing an $S = 1/2$ for each unpaired electron. Organic radicals have attracted current interests because of the emergence of novel quantum magnetic phenomena due to the highly isotropic nature of its electronic spin. There are some persistent organic radical species reported which are stabilized by π-conjugation. The π-conjugated planar molecules easily stack themselves with their π–planes parallel each other and give one-dimensional structures. Low-dimensional spin systems with small number of nearest neighbors are known to show large quantum fluctuations. As the simplest quantum spin system, the one-dimensional antiferromagnet has been extensively studied both theoretically and experimentally. Recently quantum phenomena in more complicated spin systems have shown a renewed interest.

In this study, new organic radicals were designed and synthesized to realize one-, two- and three-dimensional spin network. The author focuses on nitroxide-based materials, which have partial electric charges on the radical unit. Due to the electrostatic interaction, the intermolecular contact between the radical units is realized which results in the formation of the antiferromagnetic interaction. In order to realize high-dimensional spin network, the polyradical approach was applied. The introduction of two or three radical units within a molecule increases the number of intermolecular network path. The author also demonstrated that the large dihedral angle in a π-conjugated molecule realized the intermolecular network in multiple directions. The magnetic properties at low temperature and in magnetic field were studied with the aid of molecular orbital and numerical calculations.

This thesis consists of six chapters. Chapter 1 “General introduction” describes the research background of organic magnetic compounds and the purpose of this study. In chapter 2 “Experimental”, the general techniques of synthesis, crystal structural analysis, magnetic measurements, specific heat measurements, molecular orbital calculation, and numerical calculation were described.

Chapter 3 “Magnetic interactions and molecular packing” shows the relation between the magnetic interactions and molecular packing taking examples on the known compounds of galvinoxyl and PNNBNO. Galvinoxyl is a well-known organic mono-radical whose intermolecular ferromagnetic interaction was reported in the end of 1960’s. It is also reported that the magnetism disappeared below about 80 K due to some structural change. The ferromagnetic state of galvinoxyl was studied in the

mixed crystals and in pressure. In this study, the crystal structure at low temperature was firstly solved. The differences in the molecular packing between the high and low temperature phases were presented. The key factors of the appearance of intermolecular ferromagnetic and antiferromagnetic interactions were discussed with the aid of molecular orbital calculations.

An organic triradical PNNBNO is the first example of organic ferrimagnet but the precise study has been prevented due to its transition at low temperature (T_C = 0.28 K). The preliminary measurements of neutron scattering were done and the magnetic interactions were examined by molecular orbital calculations.

In chapter 4 "Low-dimensional organic magnets", a quasi-one-dimensional organic magnet is described. Pentafluorophenyl nitronyl nitroxide forms a one-dimensional antiferromagnetic chain and its uniform structure is lost at low temperature. Effect of the stress and behavior in magnetic field is discussed. A triangular triradical spin system, giving triangular spin tube coupled in two-dimensions, is also described.

Chapter 5, "Three-dimensional antiferromagnet F_4BIPBNN", describes the quantum properties in a three-dimensional magnet for the first time. A three-dimensional honeycomb network of S = 1/2 is formed. Two nitronyl nitroxide units linked by tetrafluorobiphenyl with a large dihedral angle between the radical unit and biphenyl due to the electrostatic repulsion between the oxygen and fluorine atoms, afford the three-dimensional network. Each S = 1/2 is surrounded by four neighboring spins with a J_0-J_1-J_1-J_2 arrangement, where J_0 is the intramolecular interaction whereas J_1 and J_2 are intermolecular interactions. The analysis of the numerical calculation gives the parameter set of J_0/k_B = 6.6 K, J_1/k_B = 4.3K and J_2/k_B = 5.9K. The temperature dependence of the susceptibility, the magnetization curves and the transition temperature (T_N = 2.7 K at magnetic field B = 0.1 T) are well reproduced by this three-dimensional model. The characteristic feature of this material is the concave shape of magnetization curve at 0.4 K, which suggests the effect of spin fluctuations. In the temperature-field phase diagram, the transition temperature decreases for B >3 T and it is almost independent on B for B < 3 T. This behavior can be related to the quantum effect in this material. This is the first observation of the quantum nature in a three-dimensional spin network.

Chapter 6 "Conclusions" summarizes the concluding remarks of the research. The magnetic properties of several organic radicals forming one-, two- and three-dimensional network were examined. The spin density distribution on the whole molecule is characteristic to organic π-conjugated molecule and responsible for the magnetic interactions. The relation between the molecular packing and intermolecular interactions were revealed. Based on the knowledge, the spin network is controlled by molecular design. The low-temperature measurements of physical properties and the analysis revealed the quantum nature of the organic radical crystals even in three-dimensional spin systems.

List of Publications

1) “Crystal dependence of the magnetic properties of an antiferromagnetic alternating chain compound F_5PNN”, Naoki Amaya, Naoya Obata, Hironori Yamaguchi, Toshio Ono, and Yuko Hosokoshi, *J. Phys.: Conf. Ser.*, **400**, 032002/1-4 (2012).

2) “Direct three-dimensional ordering of quasi-one-dimensional quantum dimer system near critical fields”, Taku Matsushita, Nobuyoshi Hori, Seiya Takata, Nobuo Wada, Naoki Amaya, and Yuko Hosokoshi, *Phys. Rev. B*, **95,** 020408/1-4 (2017). [Editors’ suggestion]

3) “Spin-1/2 quantum antiferromagnet on a three-dimensional honeycomb lattice formed by a new organic biradical F_4BIPBNN”, Naoki Amaya, Toshio Ono, Yuta Oku, Hironori Yamaguchi, Akira Matsuo, Koichi Kindo, Hiroyuki Nojiri, Fernando Palacio, Javier Campo, and Yuko Hosokoshi, *J. Phys. Soc. Jpn.*, **86**, 074706 (2017).

Supplementary List of Publications

1) “Experimental Realization of a Quantum Pentagonal Lattice”, Hironori Yamaguchi, Tsuyoshi Okubo, Shunichiro Kittaka, Toshiro Sakakibara, Koji Araki, Kenji Iwase, Naoki Amaya, Toshio Ono, and Yuko Hosokoshi, *Scientific report,* **5**, 15327/1-6 (2015).