High filed magnetization processes of BIPNNBNO and PIMBNO at low temperature

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Abstract

The magnetizations of organic spin systems BIPNNBNO and PIMBNO were measured at 400 mK in high magnetic fields up to 40 T. BIPNNBNO has a spin gap, which is closed at 4.5 T. Magnetization plateaux of 1/3 and 2/3 are found at 7-22 T and around 25 T, respectively. Above 28 T, the magnetization is completely saturated. The magnetization of PIMBNO increases super-linearly with field and saturates to 1 μ_B/f.u. above 8T.

Key words: Organic spin system; High field magnetization; Magnetization plateau; Spin frustration

There has been considerable interest in the study of low-dimensional Heisenberg quantum spin systems with frustration. In organic radicals consisting of only light elements, electron spins are isotropic and considered as ideal Heisenberg spins. Recently, Hosokoshi et al. succeeded to prepare a ferrimagnetic material with a ladder structure consisting of a triradical PNNBNO including an $S = 1$ and an $S = 1/2$ unit within a molecule [1]. These units are connected by intra- and intermolecular antiferromagnetic interactions and a 3D ferrimagnetic ordering was observed at a very low temperature 0.28 K. In the present study, we have prepared two novel frustrated spin systems composed of organic triradicals BIPNNBNO and PIMBNO [2]. The magnetization curves of both systems have been measured at 400 mK in pulsed high magnetic fields up to 40 T.

Each of the molecules BIPNNBNO and PIMBNO includes three $S = 1/2$ spins (see Figs. 2 and 3). According to the guideline for the sign of the intramolecular interaction between unpaired electrons [3], we can expect ferromagnetic and antiferromagnetic interactions, J_F and J_{AF} in the molecule. The magnitude of J_F will be vary large considering the related biradical BNO with $2J_F/k \geq 600$ K [4]. Thus, the two spins connected by J_F will behave as an $S = 1$ species.

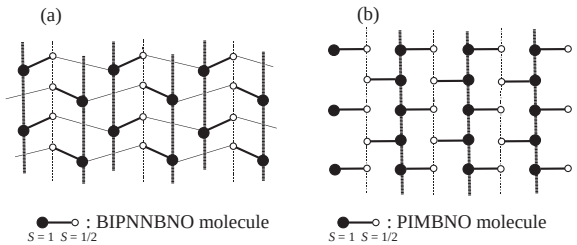

Fig. 1. Interaction networks in BIPNNBNO (a) and PIMBNO (b).

The crystal structure of BIPNNBNO is orthorhombic (*Pbcn*, $a = 9.0126(7)$ Å, $b = 17.578(1)$ Å, $c = 33.924(3)$ Å, $V = 5374.3(6)$ Å^3, $Z = 8$). Ferrimagnetic chains are formed along the b axis by the intra- and intermolecular couplings between the $S = 1$ and $S = 1/2$ spins. Along the a axis, two kinds of interchain interactions are seen. One is between the $S = 1/2$ spins, which connects the nearest neighboring chains. The other is between the $S = 1$ species, which connects the next nearest neighboring chains. These contacts will

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produce spin frustration. The interaction network of BIPNNBNO is shown in Fig. 1.

The susceptibility of BIPNNBNO increases monotonically with increasing temperature and exhibits a broad shoulder around 16 K. At 4 K it shows a sharp peak and then abruptly decreases toward zero, suggesting the existence of a spin gap. Using the susceptibility data above 20 K, the intramolecular interactions are estimated to be $2J_{\rm F}/k = 860$ K and $2J_{\rm AF}/k = -26$ K [2].

Figure 2 shows the complete magnetization process of BIPNNBNO. The magnetization is nearly zero below 4.5 T, increases rapidly above 4.5 T and shows a plateau of 1 $\mu_{\rm B}$/f.u., which corresponds to the 1/3 magnetization plateau. We consider that in the plateau region each molecule has an $S = 1/2$ spin aligned along the field direction. Above 23 T, it increases again and saturates to be 3 $\mu_{\rm B}$/f.u. at 29 T. It should be noted that a very narrow magnetization plateau of 2/3 appears around 26 T. This may be related to the spin frustration in this quasi-2D spin system.

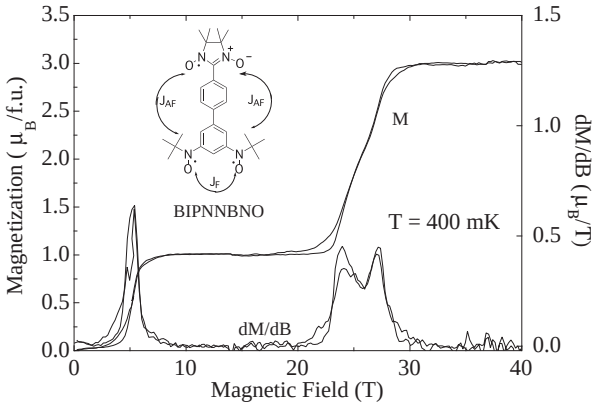

Fig. 2. Magnetization curve of BIPNNBNO.

The crystal structure of PIMBNO is monoclinic ($P2_1/m$, $a = 11.969(3)$ Å, $b = 9.499(2)$ Å, $c = 19.330(5)$ Å, $\beta = 94.50(1)^\circ$, $V = 2191.0(7)$ Å^3, $Z = 4$). The interaction network along the ab plane is shown in Fig. 1. The interaction between the networks also exist, which produces spin frustration [2]. The susceptibility increases monotonically with decreasing temperature and seems to exhibit a peak at the lowest temperature 1.8 K. The intramolecular interactions are estimated to be $2J_{\rm F}/k \sim 1000$ K and $2J_{\rm AF}/k \sim -152$ K from the susceptibility data [2].

Figure 3 shows the magnetization process of PIMBNO. The magnetization increases super-linearly with field and saturates to be 1 $\mu_{\rm B}$/f.u. above 8 T. The super-linear increase may be related to the spin frustration in this system. Since the interaction $J_{\rm AF}$ is very large compared with the applied field, the PIMBNO molecule behaves as an $S = 1/2$ spin, which is oriented along the field direction in the saturation region. In order to obtain the complete magnetization process, much higher fields are necessary.

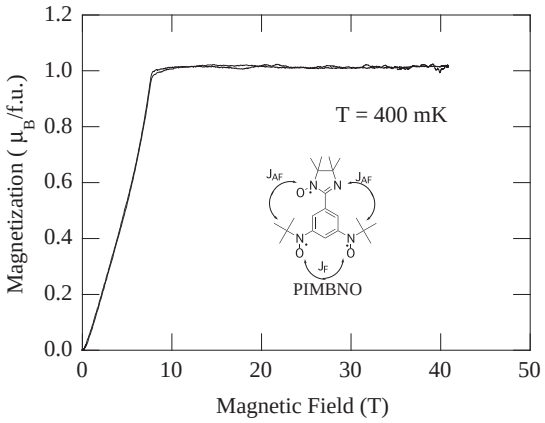

Fig. 3. Magnetization curve of PIMBNO.

In conclusion, we succeeded to prepare two novel spin system consisting of organic triradicals BIPNNBNO and PIMBNO which behave as a pair of $S = 1/2$ and $S = 1$ spins coupled antiferromagnetically. The high field magnetizations of these systems were measured at 400 mK. BIPNNBNO has a spin gap. This gap is closed at 4.5 T. The 1/3 magnetization plateau and the narrow 2/3 one are found at 7-22 T and around 25 T, respectively. Above 28 T, the magnetization is completely saturated. The magnetization of PIMBNO super-linearly increases with field and saturates to 1 $\mu_{\rm B}$/f.u. above 8T.

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