S = 1 Antiferromagnetic 1-D Heisenberg Chain of Verdazyl-Nitroxide Diradical with Long-Range Ordering and Haldane Gap

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Low-dimensional magnetism has attracted interest in light of quantum phenomena that cannot be expected from the classical picture. As a representative example, Haldane predicted that the spin excitation behavior of 1-D antiferromagnetic (AFM) Heisenberg chains strongly depends on whether *S* is an integer. Namely, spin excitation occurs with an energy gap for an integer *S*, but it becomes gapless for a half-integer *S*.[1] Metal complexes have been used as models of *S* = 1 AFM Heisenberg systems, but large spin-orbit coupling often interferes with the quantum effect. Thus, organic compounds with smaller spin-orbit coupling are promising targets. However, only two organic diradicals are known to form *S* = 1 AFM Heisenberg chain,[2,3] and the existence of the Haldane gap was not confirmed.

Herein, we synthesized a new diradical, verdazyl-nitroxide diradical **1**, and studied its magnetic properties. Diradical **1** has a triplet ground state and small magnetic anisotropy ($|D/2J| = 5.5\times10^{-5}$). In the crystal, **1** was packed in a 1-D chain manner (Figure 1c). Diradical **1** showed strong intramolecular ferromagnetic interactions (J_F/k_B = 190 K) and weak intermolecular AFM interaction (J_{AF}/k_B = –2.8 K). The *M*-*H* curve of **1** showed a hysteresis between 0–200 Oe and a plateau between 200–4000 Oe. The narrow hysteresis is attributed to the spin canting through spin-orbit coupling, indicating the existence of long-range magnetic ordering. Furthermore, the plateau indicates the gapped spin excitation, which is the first confirmation of the Haldane gap in a purely organic crystal.

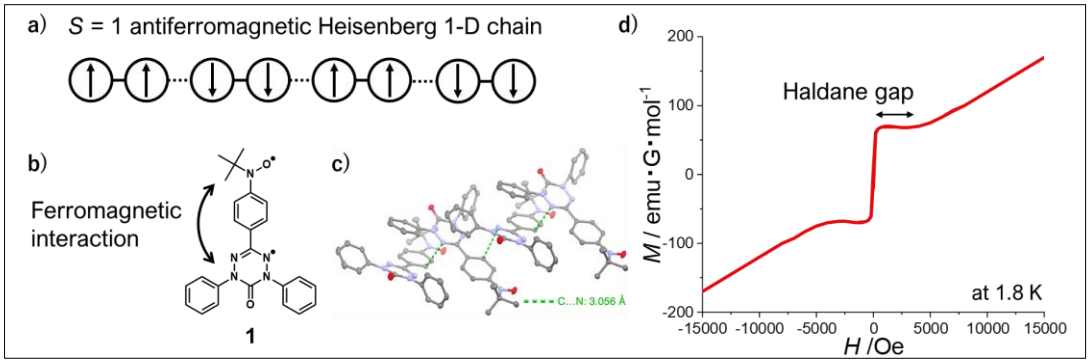

Figure 1. a) Schematic drawing of 1-D AFM Heisenberg Chain of *S* = 1 diradical, b) verdazyl-nitroxide diradical **1**, c) X-ray crystal structure of **1**, and d) *M*-*H* curve of **1**.

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