Editors' Suggestion

Candidate for a fully frustrated square lattice in a verdazyl-based salt

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We present an experimental realization of an S = 1/2 fully frustrated square lattice (FFSL) composed of a verdazyl-based salt (*p*-MePy-V)(TCNQ) · (CH₃)₂CO. *Ab initio* molecular orbital calculations indicate that there are four types of competing ferro- and antiferromagnetic nearest-neighbor interactions present in the system, which combine to form an S = 1/2 FFSL. Below room temperature, the magnetic susceptibility of the material can be considered to arise from the S = 1/2 FFSL formed by the *p*-MePy-V and indicates that the system forms a quantum valence-bond solid state whose excitation energy is gapped. Furthermore, we also observe semiconducting behavior arising from the one-dimensional chain structure of the TCNQ molecules.

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One of the current key focus areas in condensed matter physics is the search for quantum phenomena associated with quantum entanglement. Frustrated magnets, in which neighboring spins interact through competing exchange interactions that cannot be satisfied simultaneously, prevent the formation of conventional magnetic order and can form an entangled spin state. For example, the S = 1/2 antiferromagnetic (AF) triangular and kagome lattices have attracted much interest in recent decades because there are strong arguments to suggest that these systems favor the formation of a quantum spin liquid. While theoretical research on the triangular lattice has established that its ground state is an AF ordered state [1,2], the ground state of the kagome lattice is expected to realize a disordered quantum state due to its enhanced quantum fluctuations arising from the smaller coordination number (i.e., 4) [3–5]. A square lattice with nearest-neighbor interactions can also be made to exhibit frustration by introducing a competing ferromagnetic interaction. Such a system is called a fully frustrated square lattice (FFSL) and the XY model of the FFSL has been thoroughly studied in association with the separated phase transitions of spin and chirality [6–8]. The S = 1/2FFSL is also expected to exhibit strong quantum fluctuations owing to the lattice having the same coordination number as that of the kagome lattice. Furthermore, since spins are connected by a ferromagnetic interaction, this may stabilize a multimagnon bound state, yielding a hidden spin multipole order.

In order to design such a frustrated S = 1/2 quantum spin system, we have focused on the verdazyl radical, which can exhibit a delocalized π -electron spin density in nonplanar molecular structures. The flexibility of the molecular orbitals in the verdazyl radical enables one to tune the intermolecular magnetic interactions by molecular design. In fact, recently, we demonstrated that the verdazyl radical can form a variety of unconventional S = 1/2 Heisenberg spin systems, such as the ferromagnetic-leg ladder, quantum pentagon, and random honeycomb, which have not been realized in conventional inorganic materials [9–12]. Furthermore, in contrast to conventional organic radical systems, the verdazyl radical facilitates the design and formation of ferromagnetic interactions.

In this Rapid Communication, we report our findings on a realization of an S = 1/2 Heisenberg FFSL model compound $(p-MePy-V)(TCNQ) \cdot (CH_3)_2CO[p-MePy-V=3-$ (4-methylpyridyl)-1,5-diphenylverdazyl; TCNQ=7,7,8,8tetracyanoquinodimethane]. We successfully synthesized single crystals of this verdazyl-based salt and our ab initio molecular orbital (MO) calculations indicated the formation of an S = 1/2 FFSL with four types of competing nearestneighbor interactions causing the frustration. Moreover, the magnetization susceptibility below room temperature can be considered to arise from the S = 1/2 FFSL formed by the p-MePy-V and indicates the formation of a quantum valencebond solid state with a gapped excitation energy. Furthermore, we observed that the verdazyl-based salt exhibited semiconducting behavior arising from the one-dimensional (1D) chain structure of its constituent TCNQ molecules.

We prepared p-MePy-V using a conventional procedure [13] and synthesized (p-MePy-V)(TCNQ) using a reported procedure for the salts with the same chemical structure [14]. Recrystallization using ethanol in an (CH₃)₂CO atmosphere yielded the shiny brown crystal of (p-MePy-V)(TCNQ). (CH₃)₂CO. The crystal structure was determined on the basis of intensity data collected using a Rigaku AFC-7R Mercury CCD at 293 K. The magnetizations were measured using a commercial superconducting quntum interference device (SQUID) magnetometer (MPMS-XL, Quantum Design) The experimental result was corrected for the diamagnetic contribution calculated using the Pascal method. The specific heat was measured with a commercial calorimeter [physical properties measurement system (PPMS), Quantum Design] by using a thermal relaxation method. All the above experiments were performed using single crystals with typical dimensions of $0.8 \times 0.4 \times 0.2 \text{ mm}^3$. The resistivity along the *a* axis was also measured with the PPMS using the standard dc four-probe method option from 272 to 300 K. Typical dimensions of the sample were $0.74 \times 0.63 \times 0.2 \text{ mm}^3$. Four gold wires (0.025 mm diameter) bonded to the crystal with carbon paste were used as the current and voltage terminals. Ab initio

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MO calculations were performed using the unrestricted Becke three-parameter Lee-Yang-Parr (UB3LYP) functional method as broken-symmetry (BS) hybrid density functional theory calculations. All calculations were performed using the GAUS-SIAN09 software package and 6-31G basis sets. To estimate the intermolecular exchange interaction of the molecular pairs within 4.0 Å, we employed a conventional evaluation scheme [15]. We calculated the magnetic susceptibility of the S = 1/2AF chain by using the quantum Monte Carlo method. The calculation was performed for N = 256 under the periodic boundary condition, where N denotes the system size, by using the ALPS application [16–18].

The crystallographic parameters at room temperature are as follows [19]: triclinic, space group $P\bar{1}$, a = 7.851(3) Å, $c = 17.031(6) \text{ Å}, \quad \alpha = 94.579(5)^{\circ},$ $\gamma = 103.487(4)^{\circ}, \quad V = 1438.8(9) \text{ Å}^{3},$ b = 11.302(4) Å, $\beta = 99.399(4)^{\circ}$, Z = 2. The (CH₃)₂CO molecules in the crystal have two disordered CO patterns. Figure 1(a) shows the molecular structure of (*p*-MePy-V)(TCNQ), where each molecule has S = 1/2. As shown in Fig. 1(b), the crystals are seen to have a shiny surface, reflecting their conductivity. The verdazyl ring (which includes four N atoms), the upper two phenyl rings, and the bottom 4-methylpyridyl ring are labeled by R_1 , R_2 , R_3 , and R₄, respectively. The dihedral angles of R₁-R₂, R₁-R₃, R₁-R₄ are approximately 15°, 20°, and 3°, respectively. The results of our MO calculations indicate that approximately 59% of the total spin density is present on R₁, while R₂, R₃, and R₄ each account for approximately 19%, 18%, and 4% of the total spin density, respectively. Although the spin density is distributed over the molecule, we have confirmed that each verdazyl molecule can be considered to have a localized S = 1/2 in crystals from our previous quantitative studies [20-23].

The crystals include two crystallographically independent TCNQ molecules. These two molecules stack themselves in an alternating sequence with their molecular planes aligned in parallel by a translation. Each molecule has an inversion center at the central part of the molecule, yielding a 1D chain structure along the a axis, as shown in Fig. 1(c). Our MO

calculations reveal that the exchange interaction between the spins of the TCNQ molecules is given by $J_0/k_{\rm B} = 1796$ K, which is defined in the Heisenberg spin Hamiltonian given by $\mathcal{H} = J_n \sum_{\langle i,j \rangle} S_i \cdot S_j$, where $\sum_{\langle i,j \rangle}$ denotes the sum over the neighboring spin pairs. This large result is not unusual as general salts comprising the TCNQ radical are known to exhibit strong intermolecular interactions. In terms of the *p*-MePy-V molecule, the four types of overlap of the π orbitals, which expand perpendicular to the labeled planes, are expected in the ab plane, yielding a two-dimensional (2D) structure, as shown in Fig. 1(d). All molecular pairs are related by an inversion center, and the N-C and C-C short contacts for the J_1 , J_2 , J_3 , and J_4 interactions are given by 3.72, 3.63, 3.52, and 3.49 Å, respectively, as shown in Fig. 1(d). The 2D structures of the *p*-MePy-V molecules are distinctly separated by the TCNQ chains and $(CH_3)_2CO$ molecules, as shown in Fig. 1(e). Furthermore, our MO calculations show that the corresponding exchange interactions are given by $J_1/k_B = 133$ K, $J_2/k_B =$ 46 K, $J_3/k_B = 30$ K, and $J_4/k_B = -24$ K, respectively. As a consequence, the four dominant interactions form an S = 1/2FFSL in the *ab* plane, as shown in Fig. 2.

Figure 3 shows the temperature dependence of the magnetic susceptibility ($\chi = M/H$) at 0.5 T. One can observe a broad peak at approximately 100 K. If we calculate χ for the S = 1/2 AF TCNQ chain assuming the MO evaluation of $J_0/k_{\rm B} = 1796$ K, a broad peak appears at 1100 K, as shown in the inset of Fig. 3. Although this calculated χ has a finite value associated with the formation of a Tomonaga-Luttinger liquid state in the low-temperature region, its order of magnitude is approximately ten times smaller than that of the experimental value. Therefore, below the room temperature, the observed magnetization can be considered to arise from the S = 1/2FFSL formed by the *p*-MePy-V molecules. Thus, the observed broad peak is expected to be associated with the formation of a quantum state originating from the internal interactions of the FFSL. Moreover, below 100 K, χ decreases drastically with decreasing temperature, which indicates the existence of a nonmagnetic ground state separated from the excited



FIG. 1. (a) Molecular structure of (p-MePy-V)(TCNQ). (b) Single crystals of $(p-MePy-V)(TCNQ) \cdot (CH_3)_2CO$. (c) 1D chain structure composed of TCNQ radical anions. (d) 2D structure composed of p-MePy-V radical cations. (e) Crystal structure viewed parallel to the *a* axis. Hydrogen atoms are omitted for clarity. The dashed lines indicate N-C and C-C short contacts.



FIG. 2. S = 1/2 FFSL in the *ab* plane of (*p*-MePy-V)(TCNQ) · (CH₃)₂CO crystal formed by AF J_1 , J_2 , J_3 , and ferromagnetic J_4 .

states by an energy gap. We note that the upturn below ~ 20 K is caused by slight paramagnetic impurities associated with lattice defects. Assuming conventional paramagnetic behavior $C_{\rm imp}/T$, where $C_{\rm imp}$ is the Curie constant of the impurities, we evaluated the paramagnetic impurities to be approximately 0.7% of all spins, which is close to those evaluated in other verdazyl radical compounds [9,22,24], and subtracted it from the raw data, as shown in Fig. 3. Since the AF J_1 interaction is stronger than the other interactions, the ground state is expected to be a valence-bond solid with J_1 dimers. We calculated χ for the AF dimer coupled through J_1 and obtained an impressive



FIG. 3. Temperature dependence of magnetic susceptibility ($\chi = M/H$) of (*p*-MePy-V)(TCNQ) · (CH₃)₂CO at 0.5 T. The open circles denote raw data, and the solid ones are corrected for the paramagnetic term due to the impurity. The solid line represents the calculated results for the S = 1/2 AF dimer coupled through J_1 . The inset shows calculated χ in terms of the S = 1/2 1D AF chain with $J_0 = 1796$ K.



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FIG. 4. Temperature dependence of (a) specific heat C_p and (b) resistivity ρ along the *a* axis of (p-MePy-V)(TCNQ) \cdot (CH₃)₂CO.

agreement between the experiment and calculation including the gapped behavior in the low-temperature region by using $J_1/k_B = 163$ K, where we assumed g = 2.0. The obtained value of J_1 is close to that evaluated from the MO calculation; thus, we confirm that the evaluation of the interactions from the MO calculation is reliable in the present case as that in the other verdazyl compounds. By taking the interdimer frustrated interactions into consideration, other phases could be obtained by tuning external parameters such as the magnetic field and pressure.

The specific heat at zero field indicates consistent behavior with the magnetic susceptibility, as shown in Fig. 4(a). In particular, there is no sharp peak associated with a phase transition to an ordered state. Although a Schottky-like peak associated with an excitation gap is masked by the lattice contributions, an exponential decrease with decreasing temperature appears in the low-temperature region, which is consistent with the existence of an energy gap. The temperature dependence of the resistivity along the a axis is shown in Fig. 4(b), and the resistivity at room temperature is given by $2.8 \times 10^4 \ \Omega \text{ cm}$. We observed typical semiconducting behavior with an activation energy of 0.20 eV. Considering the large overlap of π orbitals of the TCNQ radical anions, this electric conductivity arises from the 1D chain structure of the TCNQ molecules. In fact, several other TCNO-based salts are also known to exhibit such semiconducting behavior and to have similar activation energies [14,25,26].

In summary, we have succeeded in synthesizing single crystals of the verdazyl-based salt (p-MePv-V)(TCNO). (CH₃)₂CO. Our *ab initio* MO calculations indicate that the *p*-MePy-V molecules form an S = 1/2 FFSL, in which four types of nearest-neighbor interactions cause frustration, while the TCNQ molecules form an S = 1/2 AF chain. Below room temperature, the magnetization susceptibility can be considered to be dominated by the S = 1/2 FFSL and indicates that the system forms a quantum valence-bond solid with an excitation energy gap. The specific heat exhibits an exponential decrease with decreasing temperature in the low-temperature region, which is consistent with the existence of an energy gap. Furthermore, we observe typical semiconducting behavior originating from the 1D chain structure of the TCNQ molecules. We note that by further consideration of the interdimer frustrated interactions and correlations between the FFSL and semiconducting 1D chain, unconventional characteristics and magnetic orderings could be observed by tuning external parameters such as the magnetic field and pressure. The present material provides a way to realize a variety of S = 1/2 FFSL through our molecular design method and will stimulate theoretical studies on FFSL.

- B. Bernu, P. Lecheminant, C. Lhuillier, and L. Pierre, Phys. Rev. B 50, 10048 (1994).
- [2] L. Capriotti, A. E. Trumper, and S. Sorella, Phys. Rev. Lett. 82, 3899 (1999).
- [3] K. Matan, T. Ono, Y. Fukumoto, T. J. Sato, J. Yamaura, M. Yano, K. Morita, and H. Tanaka, Nat. Phys. 6, 865 (2010).
- [4] T.-H. Han, J. S. Helton, S. Chu, D. G. Nocera, J. A. Rodriguez-Rivera, and C. Broholm, Nature (London) 492, 406 (2012).
- [5] S. Nishimoto, N. Shibata, and C. Hotta, Nat. Commun. 4, 2287 (2013).
- [6] M. Benakli and E. Granato, Phys. Rev. B 55, 8361 (1997).
- [7] E. H. Boubcheur and H. T. Diep, Phys. Rev. B 58, 5163 (1998).
- [8] S. Okumura, H. Yoshino, and H. Kawamura, Phys. Rev. B 83, 094429 (2011).
- [9] H. Yamaguchi, K. Iwase, T. Ono, T. Shimokawa, H. Nakano, Y. Shimura, N. Kase, S. Kittaka, T. Sakakibara, T. Kawakami, and Y. Hosokoshi, Phys. Rev. Lett. **110**, 157205 (2013).
- [10] H. Yamaguchi, H. Miyagai, T. Shimokawa, K. Iwase, T. Ono, Y. Kono, N. Kase, K. Araki, S. Kittaka, T. Sakakibara, T. Kawakami, K. Okunishi, and Y. Hosokoshi, J. Phys. Soc. Jpn. 83, 033707 (2014).
- [11] H. Yamaguchi, T. Okubo, S. Kittaka, T. Sakakibara, K. Araki, K. Iwase, N. Amaya, T. Ono, and Y. Hosokoshi, Sci. Rep. 5, 15327 (2015).
- [12] H. Yamaguchi, M. Okada, Y. Kono, S. Kittaka, T. Sakakibara, T. Okabe, Y. Iwasaki, and Y. Hosokoshi, Sci. Rep. 7, 16144 (2017).
- [13] R. Kuhn, Angew. Chem. 76, 691 (1964).
- [14] K. Mukai, S. Jinno, Y. Shimobe, N. Azuma, M. Taniguchi, Y. Misaki, K. Tanaka, K. Inoue, and Y. Hosokoshi, J. Mater. Chem. 13, 1614 (2003).
- [15] M. Shoji, K. Koizumi, Y. Kitagawa, T. Kawakami, S. Yamanaka, M. Okumura, and K. Yamaguchi, Chem. Phys. Lett. 432, 343 (2006).

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- [16] S. Todo and K. Kato, Phys. Rev. Lett. 87, 047203 (2001).
- [17] A. F. Albuquerque, F. Alet, P. Corboz, P. Dayal, A. Feiguin, L. Gamper, E. Gull, S. Gurtler, A. Honecker, R. Igarashi, M. Korner, A. Kozhevnikov, A. Lauchli, S. R. Manmana, M. Matsumoto, I. P. McCulloch, F. Michel, R. M. Noack, G. Pawlowski, L. Pollet *et al.*, J. Magn. Magn. Mater. **310**, 1187 (2007) (see also http://alps.comp-phys.org and http://wistaria.comp-phys.org/alps-looper/).
- [18] B. Bauer, L. D. Carr, H. G. Evertz, A. Feiguin, J. Freire, S. Fuchs, L. Gamper, J. Gukelberger, E. Gull, S. Guertler, A. Hehn, R. Igarashi, S. V. Isakov, D. Koop, P. N. Ma, P. Mates, H. Matsuo, O. Parcollet, G. Pawlowski, J. D. Picon *et al.*, J. Stat. Mech.: Theor. Exp. (2011) P05001.
- [19] Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition No. CCDC 1840712.
- [20] H. Yamaguchi, A. Toho, K. Iwase, T. Ono, T. Kawakami, T. Shimokawa, A. Matsuo, and Y. Hosokoshi, J. Phys. Soc. Jpn. 82, 043713 (2013).
- [21] H. Yamaguchi, T. Okubo, K. Iwase, T. Ono, Y. Kono, S. Kittaka, T. Sakakibara, A. Matsuo, K. Kindo, and Y. Hosokoshi, Phys. Rev. B 88, 174410 (2013).
- [22] H. Yamaguchi, Y. Shinpuku, T. Shimokawa, K. Iwase, T. Ono, Y. Kono, S. Kittaka, T. Sakakibara, and Y. Hosokoshi, Phys. Rev. B 91, 085117 (2015).
- [23] H. Yamaguchi, Y. Tamekuni, Y. Iwasaki, R. Otsuka, Y. Hosokoshi, T. Kida, and M. Hagiwara, Phys. Rev. B 95, 235135 (2017).
- [24] H. Yamaguchi, S. Nagata, M. Tada, K. Iwase, T. Ono, S. Nishihara, Y. Hosokoshi, T. Shimokawa, H. Nakano, H. Nojiri, A. Matsuo, K. Kindo, and T. Kawakami, Phys. Rev. B 87, 125120 (2013).
- [25] H. H. Afify, F. M. Abdel-Kerim, H. F. Aly, and A. A. Shabaka, Z. Naturforsch. **33a**, 344 (1978).
- [26] F. Kato and T. Tanaka, Bull. Chem. Soc. Jpn. 54, 1237 (1981).