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# Magnetic semiconductors: Molecular materials based on alkyl-pyridinium-substituted verdazyl radical cations and Ni(dmit)<sub>2</sub> anion

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#### Abstract

Five kinds of (1:1) and (1:3) salts of 3-(4- and 3-alkyl-pyridinium)-1,5-diphenylverdazyl (alkyl = ethyl and methyl) radical cations with Ni(dmit)<sub>2</sub> anion ([*p*-EtPyDV]<sup>+</sup>[Ni(dmit)<sub>2</sub>]<sup>-</sup> (1), [*m*-EtPyDV]<sup>+</sup>[Ni(dmit)<sub>2</sub>]<sup>-</sup> (2), [*p*-MePyDV]<sup>+</sup>[Ni(dmit)<sub>2</sub>]<sup>-</sup> (3), [*m*-MePyDV]<sup>+</sup>[Ni(dmit)<sub>2</sub>]<sup>-</sup> (4), and [*p*-MePyDV]<sup>+</sup>[Ni(dmit)<sub>2</sub>]<sub>3</sub><sup>-</sup> (5)) (dmit = 1,3-dithiol-2-thione-4,5-dithiolate) have been prepared, and the magnetic susceptibilities ( $\chi_M$ 's) have been measured between 1.8 and 300 K. The  $\chi_M$  of salt 1 can be well explained by a four-spin linear tetramer model ([*p*-EtPyDV]<sup>+</sup>-[Ni(dmit)<sub>2</sub>]<sup>-</sup>-[Ni(dmit)<sub>2</sub>]<sup>-</sup>-[*p*-EtPyDV]<sup>+</sup>) with an end exchange interaction  $2J_1/k_B = -780$  K and a central interaction  $2J_2/k_B = -200$  K. The formation of magnetic tetramer in salt 1 has been ascertained by the crystal structure analysis of 1. The  $\chi_M$  of salt 2 was explained by the sum of the contributions from: (i) a dimer system ( $2J/k_B = -320$  K) due to Ni(dmit)<sub>2</sub> anions and (ii) the one-dimensional (1D) Heisenberg ferromagnetic linear-chain system ( $2J k_B = +2.5$  K) due to verdazyl cations. The  $\chi_M$  of salt 3 is similar to that of salt 1, suggesting a formation of magnetic tetramer in salt 3. The  $\chi_M$  of salt 4 shows a broad maximum at  $T_{max} = 100 \pm 2$  K, and can be explained by a 1D Heisenberg antiferromagnetic alternating-chain model with  $2J_1/k_B = -165$  K (alternation parameter  $\alpha = J_2/J_1 = 0.6$ ). The conductivity ( $\sigma$ ) of salts 1, 2, 3 and 4 at 293 K was  $\sigma = 2.3 \times 10^{-5}$ ,  $1.1 \times 10^{-3}$ ,  $1.4 \times 10^{-5}$  and  $5.4 \times 10^{-6}$  S cm<sup>-1</sup> with an activation energy of  $E_A = 0.28$ , 0.52, 0.21 and 0.33 eV, respectively. The (1:3) salt 5 ( $\sigma = 1.0$  S cm<sup>-1</sup>,  $E_A = 0.048$  eV) showed three to five orders of magnitude higher conductivity than those of the (1:1) salts 1-4 at room temperature. All the (1:1) and (1:3) salts 1-5 are new molecular paramagnetic semiconductors.

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# 1. Introduction

Development of the molecular ferromagnet and the superconductor is two challenging targets in material science, and many studies have been performed with great success in recent years. On the other hand, examples of magnetic conductors, where the superconducting (or metallic) state and antiferromagnetic (AFM) (or ferromagnetic (FM)) order coexist in a system, are very limited because of the difficulty in molecular design of the complexes [1–5]. Especially, there has been no example of superconducting ferromagnet up to this time. It is well known that the assembled metal complexes, [Donor][M(dmit)<sub>2</sub>]<sub>n</sub> (M = Ni and Pd, and dmit = 1,3dithiol-2-thione-4,5-dithiolate), exhibit insulating, metallic and superconducting phases at low temperature under high pressure [6,7]. Two examples of magnetic

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semiconductors consisting of open-shell radical cation donor and metal complex anion acceptor have been reported for the (1:1) salt of Ni(dmit)<sub>2</sub> anion with the *p*-EPYNN (*p*-*N*-ethylpyridinium  $\alpha$ -nitronyl nitroxide) and the Me<sub>3</sub>N<sup>+</sup>-TEMPO (=*N*,*N*,*N*-trimethyl(1-oxyl-2,2,6,6-tetramethylpiperidine-4-yl)ammonium) radical cations [8,9].

Verdazyl radicals show a high chemical and thermal stability and can be isolated as solvent-free pure radicals in crystalline states [10]. The magnetic properties of these verdazyl radical crystals have been studied extensively, and several interesting magnetic properties such as ferromagnetism, weak ferromagnetism, antiferromagnetism, spin-Peierls transition, and spin frustration have been reported [11-17]. Recently, first two examples of molecular paramagnetic semiconductors consisting of verdazyl radical cation and metal complex anion have been reported for the Ni(dmit)<sub>2</sub> salts of 3-[4-(trialkylammonio)phenyl]-1,5-diphenyl-6-oxoverdazyl radical cations [18,19]. Further, we prepared the (1:1) and (1:2) salts of 3-(4- and 3-alkyl-pyridinium)-1,5-diphenylver-dazyl (alkyl = ethyl and methyl) radical cations with TCNQ anion, and found that the (1:2) salts are genuine organic paramagnetic semiconductors [20,21]. However, the examples of the molecular complexes between the open-shell radical cation and electron acceptor anion are very limited. In the present work, we prepared five kinds of (1:1) and (1:3) salts 1–5 of 3-(4and 3-alkyl-pyridinium)-1,5-diphenvlverdazyl (alkyl = ethyl and methyl) radical cations with Ni(dmit)<sub>2</sub> anion (see Fig. 1), and studied the structural, magnetic and conducting properties of these radical salts.

# 2. Experimental

## 2.1. Syntheses

The preparations of 3-(4-pyridyl)-1,5-diphenyl-verdazyl (*p*-PyDV) and 3-(3-pyridyl)-1,5-diphenyl-verdayl (*m*-PyDV) radicals were reported in a previous work [17]. The preparations of the iodide salts, 3-(4- and 3-alkyl-pyridinium)-1,5-diphenylverdazyl iodides (alkyl = ethyl and methyl), [*p*-EtPyDV]<sup>+</sup>I<sup>-</sup> (6), [*m*-EtPyDV]<sup>+</sup>I<sup>-</sup> (7), [*p*-MePyDV]<sup>+</sup>I<sup>-</sup> (8), and [*m*-MePyDV]<sup>+</sup>I<sup>-</sup> (9), were reported in previous papers [20,21].

Preparations of the charge transfer salts 1-5 are as follows.

# 2.1.1. $[p-EtPyDV]^+[Ni(dmit)_2]^-$ (1)

To stirred solution of  $[p-\text{EtPyDV}]^+[I]^-$  (47.0 mg, 0.100 mmol) in methanol (50 ml),  $[n-\text{Bu}_4\text{N}]^+[\text{Ni}(\text{dmit})_2]^-$  (69.4 mg, 0.100 mmol) in methanol (250 ml) was added and stirring was continued for 2 h under nitrogen atmosphere. The black-violet solids precipitated were filtered



 $R = C_2H_5 : [p-EtPyDV]^{+}[Ni(dmit)_2]^{-}(1)$  $R = CH_3 : [p-MePyDV]^{+}[Ni(dmit)_2]^{-}(3)$ 



 $R = C_2H_5 : [m-EtPyDV]^+[Ni(dmit)_2]^-(2)$  $R = CH_3 : [m-MePyDV]^+[Ni(dmit)_2]^-(4)$ 



 $[p-MePyDV]^+[Ni(dmit)_2]_3^-(5)$ 

Fig. 1. Chemical structures of the (1:1) and (1:3) salts of 3-(4- and 3-alkyl-pyridinium)-1,5-diphenylverdazyl radical cations (alkyl = ethyl and methyl) with Ni(dmit)<sub>2</sub> anion.

and washed with diethyl ether. Recrystallization of the residue from acetonitrile–diethyl ether afforded the product as black-violet prismatic crystals (43 mg, 54%): m.p. = 190.0–191.5 °C; UV (acetonitrile)  $\lambda_{\text{max}}$  (log  $\varepsilon$ ): 747 (3.37), 617 (3.59), 543 (4.03), 436 (4.26), 380 (4.56), 315 (4.59), 241 (4.64). *Anal.* Calc. for C<sub>27</sub>H<sub>21</sub>N<sub>5</sub>S<sub>10</sub>Ni: C, 40.80; H, 2.66; N, 8.81. Found: C, 40.58; H, 2.62; N, 8.46%.

The radical salts 2, 3, and 4 were prepared similarly.

### 2.1.2. $[m-EtPyDV]^+[Ni(dmit)_2]^-$ (2)

Dark-green powder crystals: m.p. = 199.0–201.0 °C; UV (acetonitrile)  $\lambda_{max}$  (log  $\varepsilon$ ) 735 (3.59), 625 (3.64), 443 (4.31), 389 (4.39), 314 (4.64), 240 (4.58). *Anal.* Calc. for C<sub>27</sub>H<sub>21</sub>N<sub>5</sub>S<sub>10</sub>Ni: C, 40.80; H, 2.66; N, 8.81. Found: C, 40.67; H, 2.61; N, 8.71%.

## 2.1.3. $[p-MePyDV]^+[Ni(dmit)_2]^-(3)$

Dark-green powder crystals: m.p. > 300.0 °C; UV (acetonitrile)  $\lambda_{max}$  (log  $\varepsilon$ ) 747 (3.36), 619 (3.59), 543 (4.13), 436 (4.26), 379 (4.56), 350 (4.51), 315 (4.60), 240 (4.65). *Anal*. Calc. for C<sub>26</sub>H<sub>19</sub>N<sub>5</sub>S<sub>10</sub>Ni: C, 39.99; H, 2.45; N, 8.97. Found: C, 40.82; H, 2.57; N, 9.14%.

#### 2.1.4. $[m-MePyDV]^+[Ni(dmit)_2]^-$ (4)

Black-violet powder crystals: m.p. > 300.0 °C; UV (acetonitrile)  $\lambda_{max}$  (log  $\varepsilon$ ) 736 (3.34), 619 (3.61), 439 (4.30), 392 (4.41), 315 (4.58), 241 (4.63). *Anal.* Calc. for C<sub>26</sub>H<sub>19</sub>N<sub>5</sub>S<sub>10</sub>Ni: C, 39.99; H, 2.45; N, 8.97. Found: C, 40.15; H, 2.55; N, 9.05%.

# 2.1.5. $[p-MePyDV]^+[Ni(dmit)_2]_3^-$ (5)

For the preparation of (1:3) salt **5**, the air oxidation of a solution containing the  $[p-\text{MePyDV}]^+[\text{Ni}(\text{dmit})_2]^-$ (**3**) (30 mg), acetic acid (20 ml) and acetic anhydride (20 ml) in acetone (300 ml) was carried out at room temperature [6,7]. Black fine crystals obtained show a high melting point and are insoluble in the usual organic solvents. The result of the elemental analysis indicates the formation of a (1:3) salt,  $[p-\text{MePyDV}]^+[\text{Ni}-(\text{dmit})_2]_3^-$  (**5**) [7]. M.p. > 300 °C; *Anal*. Calc. for  $C_{38}H_{19}N_5S_{30}Ni_3$ : C, 27.11; H, 1.14; N, 4.16. Found: C, 26.85; H, 1.27; N, 3.97%.

## 2.2. Measurements

The magnetic susceptibility ( $\chi_{\rm M}$ ) was measured in the temperature range of 1.8–300 K by a SQUID magnetometer. The  $\chi_{\rm M}$  of all samples has been corrected for the diamagnetic contribution ( $\chi_{\rm dia} = -0.399 \times 10^{-3}$  emu/mol for salts 1 and 2,  $-0.388 \times 10^{-3}$  emu/mol for salts 3 and 4, and  $-0.757 \times 10^{-3}$  emu/mol for salt 5), calculated by Pascal's method. The conductivity measurements of salts 1–5 were performed for the pressed pellet samples of salts, using the standard dc four-probe method.

#### 2.3. Structure determination

The X-ray measurements of the  $[p-\text{EtPyDV}]^+$ [Ni(dmit)<sub>2</sub>]<sup>-</sup> salt (1) and  $[p-\text{EtPyDV}]^+\text{I}^-$  salt (6) were carried out on a Rigaku AFC5R diffractometer with graphite-monochromated Mo K $\alpha$  ( $\lambda = 0.71069$  Å) radiations. The structure was solved by the direct method.

### 3. Results

## 3.1. UV-Vis spectra of salts 1-5

Absorption spectra of  $[m\text{-MePyDV}]^+[\text{Ni}(\text{dmit})_2]^-$  (4),  $[m\text{-MePyDV}]^+\text{I}^-$  (9), and  $[n\text{-Bu}_4\text{N}]^+[\text{Ni}(\text{dmit})_2]^-$  salts are measured in acetonitrile solvent. As shown in Fig. 2, the absorption spectrum of 4 can be well explained by the addition of  $[m\text{-MePyDV}]^+\text{I}^-$  (9) and  $[n\text{-Bu}_4\text{N}]^+[\text{Ni}(\text{dmit})_2]^-$ , suggesting the (1:1) complex formation between the  $[m\text{-MePyDV}]^+$  cation and the

Fig. 2. UV–Vis spectra of the (1:1)  $[m-MePyDV]^+[Ni(dmit)_2]^-$  salt (4) in acetonitrile.

 $[Ni(dmit)_2]^-$  anion [18]. Similarly, the absorption spectra of salts 1–3 in acetonitrile can be well explained by an addition of those of corresponding iodide salts and  $[n-Bu_4N]^+[Ni(dmit)_2]^-$ , respectively. The electronic structures of the verdazyl radical cation and Ni(dmit)\_2 anion moieties in salts 1–4 are thought to be similar to those in corresponding iodide salts 6–9 and  $[n-Bu_4N]^+[Ni(dmit)_2]^-$ , respectively. The (1:3) salt 5 crystals are insoluble in the usual organic solvents, and we could not measure the optical spectrum of salt 5 in solution.

## 3.2. Crystal structures of salts 1 and 6

The crystal structure could be determined for the  $[p-\text{EtPyDV}]^+[\text{Ni}(\text{dmit})_2]^-$  salt (1) and the  $[p-\text{EtPyDV}]^+$ - $I^-$  salt (6) (see Table 1). The crystal structures of salts 1 and 6 are shown in Fig. 3(a) and (b), respectively. The bond lengths and bond angles of verdazyl moieties (N1-N2-C1-N3-N4-C2) in salts 1 and 6 are similar to corresponding those of the neutral 1,3,5-triphenylverdazyl (TPV) (data are not shown) [22]. However, the dihedral angles (8.965° and 2.380°) between least-squares plane (N1–N2–N3–N4 plane) of verdazyl ring and those of N1- and N4-phenyl rings in salt 1 are much smaller than those of the iodide salt 6 (9.255° and 28.925°) and TPV (27.8(4)° and 40.2(4)°), respectively. In TPV, the verdazyl ring has an unsymmetrical boat configuration, with both C1 and C2 out of the nitrogen plane on the same side. C1 is displaced by only +0.099 Å, while C2 is displaced by +0.590 Å. The verdazyl ring in iodide salt 6 also shows similar structure to that of TPV. On the other hand, in salt 1, the deviations (-0.007(16) and +0.140(17) A) of C1 and C2 atoms out of N1-N2-N3-N4 plane are very small, indicating that the verdazyl molecule has planar structure.



Table 1 Crystal data, experimental conditions, and refinement details of salts 1 and 6

	[ <i>p</i> -EtPyDV] <sup>+</sup> [Ni(dmit) <sub>2</sub> ] <sup>-</sup> (1)	$[p-EtPyDV]^{+}I^{-}$ (6) $C_{21}H_{21}N_{5}I$	
Empirical formula	C27H21N5NiS10		
Formula weight	794.80	470.33	
Crystal color	black, prismatic	purple, prismatic	
Crystal system	triclinic	monoclinic	
Space group	$P\bar{1}(#2)$	$P2_1/c(#14)$	
Unit cell dimensions			
a (Å)	11.866(3)	8.771(2)	
b (Å)	16.556(4)	8.851(3)	
c (Å)	9.267(2)	26.166(2)	
α (°)	105.94(2)		
β (°)	111.93(2)	96.83(1)	
γ (°)	79.72(3)		
$V(Å^3)$	1618.0(8)	2016.8(8)	
Ζ	2	4	
$D_{\rm x} ({\rm g}{\rm cm}^{-3})$	1.631	1.549	
$\mu$ (cm <sup>-1</sup> ) (Mo K $\alpha$ )	12.74	16.04	
Crystal size/mm	$0.03 \times 0.10 \times 0.50$	$0.25 \times 0.23 \times 0.10$	
Number of reflections measured	5999	5262	
Number of unique reflections $(R_{int})$	5745 (0.079)	4641 (0.026)	
$R, R_w$	0.180, 0.221	0.067; 0.101	

The bond lengths and bond angles of the Ni(dmit)<sub>2</sub> anion in salt **1** are also similar to corresponding those in the  $[n-Bu_4N]^+[Ni(dmit)_2]^-$  salt (data are not shown) [23]. The result indicates that the Ni(dmit)<sub>2</sub> moiety in salt **1** is considered to exist as monoanion  $[Ni(dmit)_2]^$ with S = 1/2 [8]. The dihedral angles between leastsquares planes of two dmit rings in salt **1** is 4.683°, indicating the planarity of the Ni(dmit)<sub>2</sub> moiety.

Molecular packing of salt **1** is shown in Fig. 4. The unit cell of salt **1** contains two Ni(dmit)<sub>2</sub> anions and two verdazyl cations  $[p-EtPyDV]^+$ . The Ni(dmit)<sub>2</sub> anion molecules in salt **1** form a dimer ([Ni(dmit)<sub>2</sub>] (A)–[Ni(dmit)<sub>2</sub>] (B)) having intra-dimer contacts of ca. 3.6–3.8 Å (see Table 2). The dimer molecules are sandwiched between two verdazyl cation molecules, forming a linear tetramer ( $[p-EtPyDV]^+$  (A)–[Ni(dmit)<sub>2</sub>] (A)–[Ni(dmit)<sub>2</sub>] (B)– $[p-EtPyDV]^+$  (B)) in the crystal. The Ni(dmit)<sub>2</sub> anion dimers are connected to each other through short S–S contacts (S8–S9 = 3.566(4) Å, S9–S9 = 3.811(7) Å, and S5–S8 = 3.934(5) Å) between Ni(A) and Ni(C).

## 3.3. Conductivities of salts 1–5

The room-temperature conductivities ( $\sigma_{RT}$ 's) for salts **1**, **2**, **3**, and **4** are  $2.3 \times 10^{-5}$ ,  $1.1 \times 10^{-3}$ ,  $1.4 \times 10^{-5}$ , and  $5.4 \times 10^{-6}$  S cm<sup>-1</sup>, respectively, as listed in Table 3. As shown in Fig. 5, the salts **1**, **2**, **3** and **4** show semiconductive behavior with activation energy values ( $E_A$ 's) of 0.28, 0.52, 0.21 and 0.33 eV at the temperature range of 219–298, 250–283, 246–279



Fig. 3. Molecular structures of (a) the Ni salt **1** and (b) the iodide salt **6** with the atom numbering scheme.

and 269–298 K, respectively. The conductivity of the (1:3) salt **5** at 20 °C was  $\sigma = 1.0$  S cm<sup>-1</sup> with an activation energy  $E_A = 0.048$  eV (data are not shown), and is three to five orders of magnitude larger than those of the (1:1) salts 1–4.

## 3.4. Magnetic susceptibilities of salts 1–5

Fig. 6 shows a plot of  $\chi_M T$  versus T for salts 1–5. The value of  $\chi_M T$  for the [p-EtPyDV]<sup>+</sup>[Ni(dmit)<sub>2</sub>]<sup>-</sup> salt (1) is 0.243 K emu/mol at 300 K (see Table 3), and decreases



Fig. 4. Molecular packing in salt 1, showing the formation of magnetic linear tetramer, [verdazyl cation (A)–Ni(dmit)<sub>2</sub> anion (A)–Ni(dmit)<sub>2</sub> anion (B)–verdazyl cation (B)].

by lowering the temperature, indicating AFM interaction in salt **1**. As shown in Fig. 7, the  $\chi_M$  of salt **1** decreases slowly by lowering the temperature from 300 K, shows a minimum around 160 K, and increases rapidly below 20 K.

The value of  $\chi_{\rm M}T$  for the [m-EtPyDV]<sup>+</sup>[Ni(dmit)<sub>2</sub>]<sup>-</sup> salt (2) is 0.685 K emu/mol at 300 K, and is close to the sum of those (0.376 and 0.392 K emu/mol) expected for non-interacting S = 1/2 spin system with g-values  $g_{\rm V}^+ = 2.0032$  for  $[m\text{-EtPyDV}]^+\text{I}^-$  [21] and  $g_{\rm Ni}^- = 2.0472$ for  $[n-Bu_4N]^+[Ni(dmit)_2]^-$  [18], respectively, suggesting that both the spins of verdazyl cation and Ni(dmit)2 anion contribute to the magnetism of salt 2.  $\chi_{\rm M}T$  for salt 2 decreases gradually by decreasing the temperature, shows the plateau between 30 and 60 K, and increases by decreasing the temperature. Below 30 K, the susceptibility of salt 2 follows the Curie–Weiss law with a Curie constant of 0.376 K emu/mol and a positive Weiss constant of  $+2.2 \pm 0.2$  K (see Fig. 8(b)). The  $\chi_{M}T$ (0.388 K emu/mol) of salt 2 at the plateau (30-60 K) amounts to about one half of the value (0.768 emu K/mol) calculated on the basis of two S = 1/2 spins per one formula unit of the salt, as shown in Fig. 8(a). The additional susceptibility above 60 K is considered to be a thermally activated species which is nonmagnetic at lower temperatures. This magnetic contribution is tentatively assigned to the dimer of the  $Ni(dmit)_2$  radical anions. The susceptibility at lower temperatures is, therefore, attributed to the verdazyl radical cations.

The  $\chi_{\rm M}$  of the  $[p-{\rm MePyDV}]^+[{\rm Ni}({\rm dmit})_2]^-$  salt (3) decreases gradually by decreasing temperature from 300 K, and shows a minimum at about  $T_{\rm min} = 170$  K (data are not shown). The susceptibility increases by

Pertinent intermolecular contacts (r/Å) in  $[p-EtPyDV]^+[Ni(dmit)_2]^-$  (1) Ni(A)–Ni(B) Ni(A)-V(A) V(A)-V(B)Ni(A) - Ni(C)Ni-Ni > 5.00 Ni-Ni 4.278(3) N(i)-N(j) (*i*, *j* = 1,2,3,4) (r < 4.00 Å)(r < 4.00 Å)(r < 4.00 Å)(r < 5.00 Å)Ni-S10 S5-S8 3.815(4) 3.934(5) Ni-N2 3.771(9) N1-N1 4.29(2)Ni-C6 3.87(1) S8-S9 3.566(4) Ni-N3 3.684(9) S2-S7 3.970(5) S9-S9 3.811(7) S4-N1 3.936(9) S3-S7 3.614(5)S4-N3 3.69(1) S4-S8 3.819(5) S4-N4 3.30(1)S4-C5 S5-N1 3.79(1) 3.59(1) S4-C6 3.81(1) S5-N23.67(1) C2-C4 S10-N3 3.597(9) 3.63(2)C2-N1 3.62(2) C2-N4 3.90(1)

C3-N1

3.56(1)

Table 3

Table 2

Conductivity ( $\sigma_{RT}$ ), activation energy ( $E_A$ ),  $\chi_M T$  value (at 300 K), and magnetism of salts 1–5

Salts	$\sigma_{\rm RT}~({\rm S~cm^{-1}})$	$E_A$ (eV)	$\chi_{\rm M}T$ (K emu/mol)	magnetism
[ <i>p</i> -EtPyDV] <sup>+</sup> [Ni(dmit) <sub>2</sub> ] <sup>-</sup> (1)	$2.3 \times 10^{-5}$	0.28	0.243	linear tetramer
				$(2J_1k_B = -780 \text{ K}, 2J_2k_B = -200 \text{ K}) + \text{Curie impurity} (5.3\%)$
$[m-\text{EtPyDV}]^+[\text{Ni}(\text{dmit})_2]^-$ (2)	$1.1 \times 10^{-3}$	0.52	0.685	1D-Ferro $(2J/k_{\rm B} = +2.5 \text{ K}) + \text{S}-\text{T} (2J/k_{\rm B} = -320 \text{ K})$
$[p-MePyDV]^+[Ni(dmit)_2]^-$ (3)	$1.4 \times 10^{-5}$	0.21	0.288	linear tetramer
$[m-\text{MePyDV}]^+[\text{Ni}(\text{dmit})_2]^-$ (4)	$5.4 \times 10^{-6}$	0.33	0.713	alternating chain ( $T_{\text{max}} = 100 \pm 2 \text{ K}, 2J_1k_B = -165 \text{ K},$
				$\alpha = J_2 J_1 = 0.6) + Curie$ impurity (5.4%)
$[p-MePyDV]^{+}[Ni(dmit)_{2}]_{3}^{-}$ (5)	1.0	0.048	0.641	Curie–Weiss law ( $C = 0.684$ (emu K)/mol, $\theta = -17$ K)



Fig. 5. Temperature dependence of the resistivity ( $\rho$ ) of the (1:1) salts **1–4** at ambient pressure.



Fig. 6. Temperature dependence of the product  $\chi_{\rm M}T$  for salts 1–5.

decreasing temperature below 170 K. The value of  $\chi_M T$  for **3** is 0.288 K emu/mol at 300 K, and decreases by lowering the temperature, indicating AFM interaction in **3**, as shown in Fig. 6. The magnetic behavior of salt **3** is very similar to that of salt **1**.

The  $\chi_{\rm M}$  of the [m-MePyDV]<sup>+</sup>[Ni(dmit)<sub>2</sub>]<sup>-</sup> salt (4) shows a broad maximum at  $T_{\rm max} = 100 \pm 2$  K, as shown in Fig. 9. An increase in susceptibility below 26 K was observed, which is probably due to Curie impurities. The value (0.713 K emu/mol) of  $\chi_{\rm M}T$  at 300 K observed for salt 4 is similar to the sum of those (0.376 and 0.392 K emu/mol) for S = 1/2 spin system with  $g_{\rm V}^+ = 2.0033$  [21] and  $g_{\rm Ni}^- = 2.0472$  [18], suggesting that both the spins of verdazyl cation and [Ni(dmit)<sub>2</sub>]<sup>-</sup> anion contribute to the magnetism of salt 4.



Fig. 7. (a) Temperature dependence of the magnetic susceptibility of salt **1**. The solid curve is the theoretical susceptibility calculated using Eq. (2) in [24]. (b) Scheme 1.

The  $\chi_{\rm M}$  of the  $[p\text{-MePyDV}]^+[{\rm Ni}({\rm dmit})_2]_3^-$  salt (5) increases monotonically by lowering the temperature, and follows the Curie–Weiss law with C = 0.684 K emu/mol and  $\theta = -17.0$  K.

## 4. Discussion

## 4.1. Magnetic properties of salts 1 and 3

The  $\chi_{M}$  of salt 1 is shown in Fig. 7. As described in a previous section, the Ni(dmit)<sub>2</sub> anion molecules in salt 1 form a dimer (Ni(dmit)<sub>2</sub> (A)-Ni(dmit)<sub>2</sub> (B)) with short intra-dimer contacts of ca. 3.6-3.7 Å, suggesting strong AFM exchange interaction. However, the  $\chi_{\rm M}$  of 1 can not be explained by a simple dimer model. In salt 1, the dimer molecules are sandwiched between two verdazyl cation molecules, forming linear tetramer  $([p-EtPyDV]^+ (A)-[Ni(dmit)_2]^- (A)-[Ni(dmit)_2]^- (B) [p-\text{EtPyDV}]^+$  (B)) (see Fig. 4 and Table 2). As described in a previous section, the verdazyl cation molecule in salt 1 has planar structure, and we can expect close contacts between verdazyl cation and Ni(dmit)<sub>2</sub> anion molecules. In fact, there are many short contacts between the Ni, S(i) and C(i) atoms in the Ni(dmit)<sub>2</sub> anions and the N(i) atoms (i = 1, 2, 3, and 4) in the hydrazidinyl moiety (N1–N2–C7–N3–N4–C8), having large unpaired spin densities, of verdazyl cations [17]. The result suggests strong exchange interaction between the verdazyl cation and the Ni(dmit)<sub>2</sub> anion molecules.



Fig. 8. (a) Temperature dependence of the product  $\chi_M T$  ( $\bigcirc$ ) for salt **2**. The solid curve is the theoretical susceptibility calculated using Eq. (2). (b) Inverse molar magnetic susceptibility ( $1/\chi_M$ ) of salt **2** at low temperatures. The observed values (open circles) obey the theoretical results for the 1D isotropic Heisenberg ferromagnet (Eq. (3)) with  $2J/k_B = +2.5$  K indicated by the solid line.



Fig. 9. Temperature dependence of the magnetic susceptibility  $(\chi_M)$  (O) of salt **4**. The dashed curve is the theoretical susceptibility calculated by using Eq. (5).

In such a case, the  $\chi_M$  of salt 1 may be explained by a four-spin Heisenberg Hamiltonian,

$$H = -2J_1(S_1S_2 + S_3S_4) - 2J_2S_2S_3,$$
  

$$S_1 = S_2 = S_3 = S_4 = 1/2,$$
(1)

where  $J_1$  is the exchange interaction between an edge verdazyl cation and a central Ni(dmit)<sub>2</sub> anion and  $J_2$  is the interaction between two central  $Ni(dmit)_2$  anions. The model is shown in Fig. 7(b). This Hamiltonian has been solved exactly by Rubenacker et al. [24] to obtain the energy levels and magnetic susceptibility. Using the Eq. (2) in [24], we have fitted our data to this model, where the g-value (g = 2.0221 at 300 K) observed for salt 1 was used tentatively for the calculation of the susceptibility. The calculated susceptibility is shown by solid curve in Fig. 7(a). The best fit parameters obtained are  $2J_1/k_B = -780$  K and  $2J_2/k_B = -200$  K. The  $2J_2/k_B$  value (-200 K) for the dimer is similar to that (-320 K)for the  $Ni(dmit)_2$  dimer in salt 2, as described later. The Ni(dmit)<sub>2</sub> (A) molecule connects with the Ni(dmit)<sub>2</sub> (C) molecule with short inter-dimer  $S \cdots S$  contacts (see Fig. 4 and Table 2). Therefore, we can expect some interaction between two Ni(dmit)<sub>2</sub> molecules (A) and (C). The difference between the experimental and theoretical values of susceptibility of salt 1 may be due to such an interaction.

The susceptibility of the  $[p-\text{MePyDP}]^+[\text{Ni}(\text{dmit})_2]^$ salt (3) is similar to that of salt 1. The result suggests that salt 3 also forms a magnetic linear tetramer as observed for salt 1.

## 4.2. Magnetic property of salt 2

The susceptibility of salt 2 can be explained by the two term contributions (Eq. (2)).

$$\chi_{\rm M} = \chi_{\rm 1D-Ferro} + \chi_{\rm S-T},\tag{2}$$

where the first and second terms represent the contributions from quasi one-dimensional (1D) FM Heisenberg linear-chain system [25] and singlet–triplet (S–T) equilibrium system, respectively.  $\chi_{1D-Ferro}$  and  $\chi_{S-T}$  are given by Eqs. (3) and (4), respectively.

$$\chi_{1\text{D-Ferro}} = (N_o g^2 \mu_{\text{B}}^2 / 4k_{\text{B}} T) [1 + (J/k_{\text{B}} T)], \qquad (3)$$

$$\chi_{\rm S-T} = (N_o g^2 \mu_{\rm B}^2 / k_{\rm B} T) [1/(3 + e^{-2J/k_{\rm B} T})]. \tag{4}$$

The susceptibility of salt **2** follows the Curie–Weiss law with positive Weiss constant of +2.2 K in the temperature region between 10 and 40 K. A plot of  $1/\chi_{\rm M}$  against *T* is no longer linear at low temperature (<10 K). Therefore, the low-temperature behavior of the susceptibility of salt **2** was analyzed on the basis of the quasi-1D FM Heisenberg model. In fact, the susceptibilities of salt **2** below 40 K are well reproduced by Eq. (3) with  $2J/k_{\rm B}$ = +2.5 ± 1.0 K and g = 2.00, as shown in Fig. 8(b). Above ca. 50 K, however,  $\chi_{\rm M}$ T increases with increasing temperature, as shown in Fig. 8(a). This increase indicates that thermal magnetic excitation occurs in addition to the 1D FM linear-chain spins. The experimental data are interpreted by the S–T model (Eq. (4)) with  $2J/k_{\rm B} =$ -320 K. As shown in Fig. 8(a), the experimental curve can be well reproduced by Eq. (2).

## 4.3. Magnetic property of salt 4

The susceptibility of salt **4** shows a broad maximum at  $T_{\text{max}} = 100 \pm 2$  K. The susceptibility of **4** can be well explained by the sum of the two contributions;

$$\chi_{\rm M} = C_{\rm 1D-Alt} \chi_{\rm 1D-Alt} + C_{\rm Curie} \chi_{\rm Curie}, \tag{5}$$

where  $C_{1\text{D-Alt}} + C_{\text{Curie}} = 2$ , and the first and second terms represent the contributions from the 1D AFM Heisenberg alternating-chain system [26] and from the Curie impurity, respectively.  $C_i$  is the fraction of each term. The dashed curve in Fig. 9 is a theoretical curve with  $C_{1\text{D-Alt}} = 2 \times 0.973$  and  $C_{\text{Curie}} = 2 \times 0.027$  and  $2J_1/k_{\text{B}} = -165$  K (alternation parameter  $\alpha = J_2/J_1 =$ 0.6). The result shows that both the spins of verdazyl cation and Ni(dmit)<sub>2</sub> anion contribute to the magnetism of salt **4**.

#### 4.4. Conducting properties of salts 1–5

Recently, we prepared several kinds of (1:1) and (1:3) salts of open-shell 6-oxoverdazyl radical cations with Ni(dmit)<sub>2</sub> anion, and found that the (1:3) salts are molecular paramagnetic semiconductors [18,19]. On the other hand, the (1:1) salts showed the property as paramagnetic insulators, as observed for the usual (1:1) salts of Ni(dmit)<sub>2</sub> anion with closed-shell electron donor cations, such as tetra-alkyl-ammonium cations, alkali metal cations, etc [6,7].

However, in the present work, all the (1:1) salts 1-4studied were found to be semiconductors, against to our expectation. As described above, salt 1 forms a magnetic linear tetramer in which the strong exchange interaction between Ni(dmit)<sub>2</sub> (A) and verdazyl (B) spins in addition to that between Ni(dmit)<sub>2</sub> (A) and (B) spins was observed. Such an interaction will induce a delocalization of conduction electron from Ni(dmit)<sub>2</sub> dimer moieties to verdazyl moieties, and, thus, a decrease in the on-site Coulomb repulsion. Further, comparatively short S–S contacts were observed between  $Ni(dmit)_2$ (A) and (C) anions, as listed in Table 2. As a result, salt 1 may show semiconductive behavior. Salt 3 showed the magnetic property similar to that of salt 1. Further, strong interaction between verdazyl cation and Ni(dmit)<sub>2</sub> anion was observed for salt 4, suggesting a decrease in the on-site Coulomb repulsion in 4. The crystal structure analyses will be necessary to discuss the details of the semiconductive behavior observed for the (1:1) salts 2-4. On the other hand, the conductivity of the (1:3) salt

**5** at 20 °C was  $\sigma = 1.0$  S cm<sup>-1</sup> with an activation energy  $E_A = 0.048$  eV. This value is three to five orders of magnitude larger than those of the (1:1) salts 1–4.

The examples of the organic/inorganic hybrid system which shows the magnetism and conductivity are very limited, because of the difficulty in molecular design of the complexes. The present work provides five examples of new molecular magnetic semiconductors consisting of open-shell verdazyl radical cation and metal complex anion. Especially, FM interaction was observed for salt **2** at 1.8–40 K. We may expect FM order for salt **2** at lower temperature.

## 5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, deposition number CCDC No. 249719. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, fax: +44 1223 336 033, e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc. cam.ac.uk), or on the web http://www.ccdc.cam.ac.uk.

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