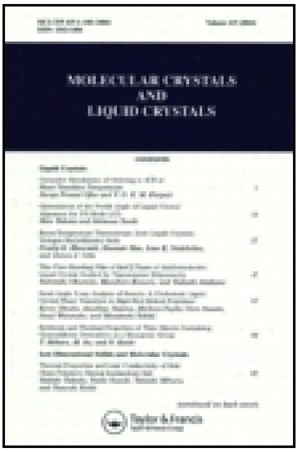

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Syntheses and Magnetic Property of the Salts of Positively-Charged Verdazyl Radicals and TCNQF 4 - Anion Radical

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To cite this article: Nagao Azuma, Nobuyoshi Senba, Kazuki Okuda, Keishi Ohara, Yuko Hosokoshi, Katsuya Inoue & Kazuo Mukai (2002): Syntheses and Magnetic Property of the Salts of Positively-Charged Verdazyl Radicals and TCNQF 4 - Anion Radical, Molecular Crystals and Liquid Crystals, 376:1, 341-346

To link to this article: http://dx.doi.org/10.1080/713738454

Mol. Cryst. Liq. Cryst., Vol. 376, pp. 341-346
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1058-725X/02 $12.00 + .00

Syntheses and Magnetic Property of the Salts of Positively-Charged Verdazyl Radicals and $TCNQF_4^-$ Anion Radical

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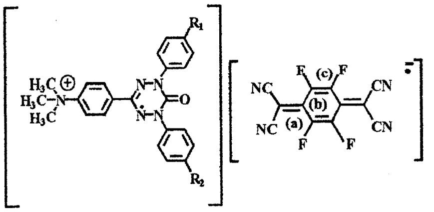
Three kinds of (1:1) salts of $TCNQF_4$ anion with 3-(4-trimethylaminophenyl)-1,5-diphenyl-6-oxo-verdazyl radical cation [1^+] and its mono-methyl [2^+] and di-methyl [3^+] derivatives have been prepared, and magnetic property and crystal structure of the salts have been studied. The salts were found to be new genuine organic magnetic compounds consisting of open-shell verdazyl radical cation and electron acceptor $TCNQF_4$ anion.

Keywords: verdazyl radical; $TCNQF_4$; magnetism; crystal structure.

INTRODUCTION

The development of organic ferromagnet and superconductor is two challenging problems, and many studies have been performed with great success in recent years. On the other hand, the examples of magnetic conductors that the magnetic order and superconducting state coexist in a system are very limited, because of the difficulty in molecular design of the complexes.[1, 2] Further, the examples of the magnetic conductor consisting of purely organic compounds have not been reported.

In the present work, we prepared 3 kinds of (1:1) salts (1), (2), and (3) of $TCNQF_4$ with 3-(4-trimethylaminophenyl)-1,5-diphenyl-6-oxo-verdazyl radical cation [1^+] and its mono- and di-methyl derivatives [2^+] and [3^+] (see Fig. 1), and studied the magnetic property and crystal structure of these radical salts, as the first step to develop new materials based on open-shell radical cation and electron acceptor anion in which the magnetic spin and conduction electron coexist.



[1]$^+$: (R$_1$ = H, R$_2$ = H)

[2]$^+$: (R$_1$ = H, R$_2$ = CH$_3$) **[TCNQF$_4^-$]**

[3]$^+$: (R$_1$ = CH$_3$, R$_2$ = CH$_3$)

FIGURE 1: Chemical structure of the salts of verdazyl with TCNQF$_4$

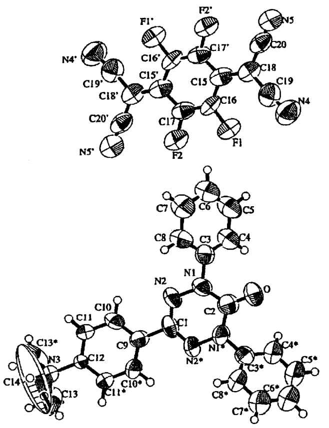


FIGURE 2: Molecular structure of the salt (1) with the atom labeling scheme.

EXPERIMENTAL

[1$^+$][TCNQF$_4^-$] (1). To solution of TCNQF$_4$ (51mg, 0.18mmol) in acetonitrile (20ml), [1$^+$][I$^-$] [3] (100mg, 0.20mmol) in acetonitrile (10ml) was added slowly. The reaction mixture was kept under dark at room temperature for one week. The crystals precipitated was filtered and washed with diethyl ether. Black-violet plate crystals (66mg, 54%): Mp 212 – 214°C; UV (acetonitrile) λ_{max} (log ε) 855 (4.54), 753 (4.22), 687 (3.68), 533 (3.32), 411 (4.62), 315 (4.16), 256 (4.33), 231 (4.36). Found: C, 63.58; H, 3.57; N, 19.05%. Calcd for $C_{35}H_{23}N_9OF_4$: C, 63.53; H, 3.50; N, 19.06%.

The following radical salts were prepared similarly.

[2$^+$][TCNQF$_4^-$] (2). Black-violet thin needle crystals: Mp. 184 - 186°C; UV (acetonitrile) λ_{max} (log ε) 855 (4.58), 753 (4.25), 687 (3.69), 535 (3.38), 411 (4.65), 319 (4.17), 256 (4.34), 232 (4.42). Found: C, 62.97; H, 3.83; N, 18.00%. Calcd for $C_{36}H_{25}N_9OF_4$: C, 63.99; H, 3.73; N, 18.66%.

[3$^+$][TCNQF$_4^-$] (3). Black-violet thin plate crystals: Mp. 196 - 198°C; UV (acetonitrile) λ_{max} (log ε) 855 (4.55), 753 (4.23), 687 (3.67), 538 (3.39), 411 (4.63), 323 (4.17), 258 (4.32), 232 (4.41). Found: C, 64.39; H, 3.92; N, 18.14%. Calcd for $C_{37}H_{27}N_9OF_4$: C, 64.43; H, 3.95; N, 18.28%.

RESULTS AND DISCUSSION

Absorption spectra of [1$^+$][TCNQF$_4^-$] (1), [1$^+$][I$^-$], and [Li$^+$][TCNQF$_4^-$] salts

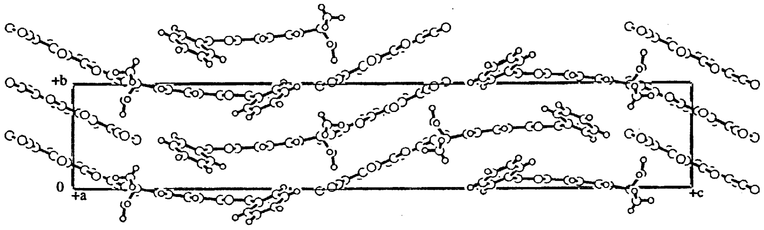


FIGURE 3: Molecular packing of the [1^+][TCNQF$_4$] salt.

were measured in acetonitrile solvents. The absorption spectrum of the [1^+][TCNQF$_4^-$] can be well explained by an addition of those of [1^+][I^-] and [Li^+][TCNQF$_4^-$], suggesting the (1:1) complex formation between [1^+] cation and [TCNQF$_4^-$] anion.[4] Similarly, the spectra of [2^+][TCNQF$_4^-$] (2) and [3^+][TCNQF$_4^-$] (3) salts can be explained by an addition of those of corresponding iodide salts and [Li^+][TCNQF$_4^-$] salt.

The crystal structure could be determined for the salt (1). Crystal data obtained for the salt (1) are as follows; orthorhombic, space group *Cmca*, a = 21.68(3), b = 7.21(2), c = 42.1(2)Å, V = 6579 Å^3, Z = 8. In Fig. 2 we show the solid state structure of salt (1). Atom numbering scheme and molecular conformation of verdazyl radical and TCNQF$_4$ are shown in Fig. 2. Molecular packing of the salt (1) is shown in Fig. 3.

There is no significant change in the bond lengths and bond angles of the central hydrazidinyl moiety, N1-N2-C1-N2*-N1*, and 4-trimethylaminophenyl ring of the verdazyl cations [1^+] in [1^+][TCNQF$_4^-$] and [1^+][I^-] salts (data are not shown). By comparing the bond lengths of TCNQF$_4$ ((a) = 1.39, (b) 1.42, and (c) = 1.34Å, see Fig. 1) in [1^+][TCNQF$_4^-$] with those of neutral TCNQF$_4$ ((a) = 1.35, (b) = 1.43, and (c) = 1.32Å) and monoanion TCNQF$_4^-$ ((a) = 1.42, (b) = 1.40, and (c) = 1.35Å), TCNQF$_4$ is considered to exist as TCNQF$_4^-$ in the salt.[5, 6]

As shown in Fig. 3, the verdazyl cation and the TCNQF$_4$ anion molecules form segregated one-dimensional (1D) columns along the b-axis with moderately short intermolecular distances. The short N...N contacts found between the nitrogen atoms in the central hydrazidinyl moiety N1-N2-C1-N2*-N1*, having the large unpaired spin densities,[7] are N1...N2 (3.83(1)Å), N2...N1 (3.89(1)Å), and N2...N2 (3.60(1)Å). Pertinent

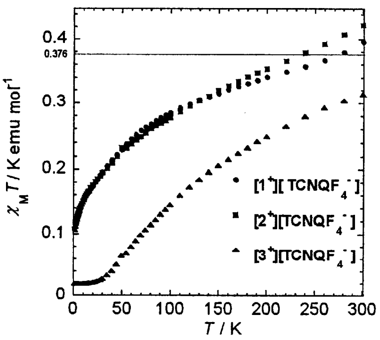


FIGURE 4: $\chi_M T$ vs. T plot for the salts (1), (2) and (3).

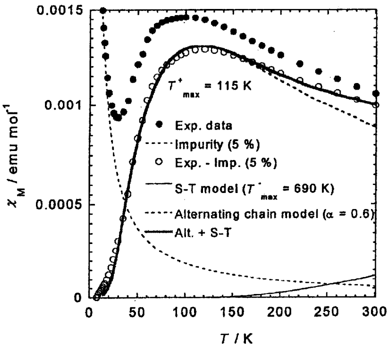


FIGURE 5: Magnetic susceptibility of the salt (3).

intermolecular distances between TCNQF$_4$ molecules are F1...F2 (3.145(7) Å), F2...C16 (3.202(9) Å), C17...C17 (3.22(2) Å), etc., showing strong contacts. The spin-spin exchange interactions ($2J_1/k_B$) and ($2J_2/k_B$) between verdazyl molecules and between TCNQF$_4$ anion molecules, respectively, are expected to be most effective along the *b*-axis.

Figure 4 shows a plot of $\chi_M T$ versus T for 3 kinds of salts. The susceptibilities of the salts have been corrected for the diamagnetic contributions, χ_{dia}= -0.327×10^{-3} (1), -0.342×10^{-3} (2), and -0.357×10^{-3} (3) emu/mol, calculated by Pascal's method. The values of $\chi_M T$ for the salts at 300 K are 0.396, 0.421, and 0.313 K emu/mol, respectively, and decrease by lowering the temperature, indicating antiferromagnetic (AFM) interaction in these salts. The values of $\chi_M T$ at 300 K are close to or smaller than that (0.376 K emu/mol) expected for non-interacting S = 1/2 radical molecules. This can be readily understood by considering that the spin of TCNQF$_4$ radical anion disappears as a result of strong AFM interaction with the neighboring spin, forming (i) a dimer in the crystal as reported for the TCNQF$_4$ salts in previous works[5, 6] or (ii) 1D magnetic linear chain as found for the salt (1) in the present work. Therefore, the susceptibilities of these salts will be mainly due to the spins of verdazyl radical cation.

We can expect that the susceptibility of the salt (1) may be described by a 1D Heisenberg AFM linear chain model, because the verdazyl radical molecule packs along b-axis forming 1D magnetic linear chain. In fact, $\chi_M T$ decreases gradually by lowering the temperature from 300 K, suggesting strong exchange interaction ($2J_1/k_B$) between verdazyl molecules. However, the susceptibility of the salt (1) does not show any peak in the temperature region 1.8 - 300 K. Further, the observed value (0.105 K emu mol^{-1}) of $\chi_M T$ at 1.8 K is larger than that expected for the Curie impurity. The magnetic property of the salt (1) is not clear at present. The temperature dependence of susceptibility of the salt (2) is similar to that of the salt (1), as shown in Fig. 4.

The susceptibility of the salt (3) shows a broad maximum at $T_{max}= 100 \pm 5$ K, as shown in Fig. 5. An increase in susceptibility below 30 K was observed, which is probably due to isolated radicals. The susceptibility can be explained by the three term contributions (Eq.(1)).

$$\chi_M = C_{1D\text{-Alt}}\chi_{1D\text{-Alt}} + C_{S\text{-}T}\chi_{S\text{-}T} + C_{Curie}\chi_{Curie} \qquad (1)$$

where $C_{1D\text{-Alt}} + C_{S\text{-}T} + C_{Curie} = 2$, and the first, second and third terms represent the contributions from one-dimensional (1D) Heisenberg AFM alternating-chain system,[8] singlet-triplet (S-T) equilibrium system, and Curie impurity, respectively. C_i is the fraction of each term. At low temperature region (T<120 K), the susceptibility for the salt (3) can be well reproduced by the two term contributions ($\chi_{1D\text{-Alt}}$ and χ_{Curie}) with the value of $C_{1D\text{-Alt}} = 0.975$ and $C_{Curie} = 0.050$ and with $2J_1/k_B = -190$ K (alternation parameter $\alpha = J_2/J_1 = 0.6$), as shown in Fig. 5. Above ca. 120 K, however, χ_M of the salt (3) cannot be explained by the first and third terms in Eq. (1), as shown in Fig. 5. The result indicates that thermal magnetic excitation arising from TCNQF$_4$ anion dimers occurs in addition to the alternating-chain spins and the Curie spins. The experimental data are interpreted by the singlet-triplet equilibrium model with the value of $2J_2/k_B = -1.61T_{max} = -1110$ K ($T_{max}= 689$ K) and $C_{S\text{-}T}= 0.975$. As shown in Fig. 5, the experimental curve can be well reproduced by Eq. (1). The present result suggests that the verdazyl cation and the TCNQF$_4$ anion molecules form segregated columns in the crystal.

The preparation of the charge-transfer complexes of 2-(4-alkyl-pyridinium)-imidazolin-1-oxyls (alkyl = Me, Et, n-Pr, and n-Bu) and 2-(3- and 4-methyl-pyridinium)-nitronylnitroxide with electron acceptors (TCNQ and $TCNQF_4$) has been reported.[5, 6] However, the electric conductivity of these complexes has not been reported. Recently, we reported that the (1:2) salts between 3-(3- and 4-ethyl-pyridinyl)-1,5-diphenyl-verdazyl radical cation and TCNQ anion show a property as magnetic semiconductor.[4] Therefore, the preparation of the (1:2) salt between verdazyl radical cations ([1^+], [2^+], and [3^+]) and $TCNQF_4$ anion is now in progress.

As a conclusion, the present result shows that the three salts (1), (2), and (3) are new genuine organic magnetic salts consisting of open-shell verdazyl radical cation and electron acceptor $TCNQF_4$ anion.

Acknowledgments

This work was partly supported by the Grant-in-Aid for Scientific Research on Priority Areas (B) of Molecular Conductors and Magnets (Area No. 730/11224205) from the Ministry of Education, Science, Sports and Culture, Japan.

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