

$2k_F$ transitions in a series of $(\text{DMET})_2(\text{X}_1\text{X}_2\text{TCNQ})$ ($\text{X}_1, \text{X}_2 = \text{Br}, \text{Cl}, \text{F}, \text{CH}_3, \text{H}$): Subsidiary lattice effect by anion radicals

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Structural and magnetic properties were investigated in a series of isomorphous 2:1 donor-acceptor-type organic charge-transfer (CT) complexes of $(\text{DMET})_2(\text{X}_1\text{X}_2\text{TCNQ})$ [DMET denotes dimethyl(ethylenedithio)diselenadithiafulvalene, TCNQ denotes tetracyanoquinodimethane, $\text{X}_1, \text{X}_2 = \text{Br}, \text{Cl}, \text{F}, \text{CH}_3, \text{H}$]. In these complexes, donors (D 's) formed quasi-one-dimensional (Q1D) molecular stacks ($D = +1/2$), which were bridged with each other, by acceptor molecules whose molecular planes were parallel to the stacking axes. By the magnetic measurements, we found that the compounds could be classified into two groups in terms of the $2k_F$ transitions of the donor stacks: two complexes exhibited the transitions at around room temperature, while the other two at lower temperature below 10 K. We discuss the origin of the difference in the observed $2k_F$ transitions in terms of the subsidiary lattice effect by the acceptor molecules on the Q1D donor stacks.

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I. INTRODUCTION

Ion-radical molecular solids provide a wide spectrum of conducting and semiconducting material that has attracted considerable attentions in solid-state physics and chemistry.¹ In particular, quasi-one-dimensional (Q1D) molecular stacks with 1/4-filling electronic bands are known to exhibit a rich variety of electronic phases, ranging from insulator to metal that involve various phase transitions; superconductivity, spin-density wave (SDW) formations, spin Peierls transitions, and Mott-Hubbard transitions.² Furthermore, recent discovery of superconductivity in $(\text{TMTTF})_2\text{PF}_6$ (TMTTF denotes tetramethyltetrafulvalene) under hydrostatic pressure above 5 GPa has revealed the relationship between the spin Peierls state and the superconducting state.³ It was also discussed that the $2k_F$ lattice distortions (period of 4 molecules) as in the spin-Peierls state coexist with various phase angles of $2k_F$ charge-density modulation, associated with the correlation effect among electrons.⁴⁻⁶ In order to achieve further understanding of such Q1D systems, it is necessary to control the $2k_F$ lattice instability, which is associated both with conducting and insulating materials through the Peierls and/or spin Peierls mechanisms.

Here we report that combinations of electron donor dimethyl(ethylenedithio)diselenadithiafulvalenes (DMET's) and four kinds of electron acceptor TCNQ derivatives, presented in Fig. 1, afford a novel isomorphous series of organic charge-transfer (CT) complexes with donor-based 1/4-filling ($D = +1/2$) Q1D stacks. The feature of such donor-acceptor-type CT complexes is that both of the donor and acceptor elements can contribute to the conducting and magnetic properties.⁷ In the $(\text{DMET})_2(\text{X}_1\text{X}_2\text{TCNQ})$ ($\text{X}_1, \text{X}_2 = \text{Br}, \text{Cl}, \text{F}, \text{CH}_3, \text{H}$) family presented in this study, the donors formed strongly dimerized Q1D stacks, while the acceptors were completely ionized, and located at the position to bridge the donor stacks. In the static magnetic and electron paramag-

netic resonance (EPR) measurements, we found that the compounds could be classified into two groups, in terms of the $2k_F$ transitions of the donor stacks. We show that the appreciable difference in the magnetic properties of the donor stacks is associated with the subsidiary lattice effect of the anion radicals. On the basis of the results, we also discuss about the transfer from the regular Peierls to the spin-Peierls transitions in the 1/4-filling Q1D Mott-Hubbard-type organic semiconductors.

II. EXPERIMENT

DMET and TCNQ derivatives ($\text{X}_1\text{X}_2\text{TCNQ}$; $\text{X}_1, \text{X}_2 = \text{Br}, \text{Cl}, \text{F}, \text{CH}_3, \text{H}$) were synthesized according to the literature.^{7,8} The CT complexes of $(\text{DMET})_2(\text{X}_1\text{X}_2\text{TCNQ})$ were prepared by the reaction of the constituent molecules in chlorobenzene. Temperature-controlled slow cooling of the reaction solution for a few days led to the crystallization of the product. The room temperature structure was determined with imaging plate diffractometer (Rigaku, RAXIS) using $\text{Mo}(K\alpha)$ radiation. The calculations were performed with the TEXSAN crystallographic software package of Molecular Structure Corporation.⁹ The magnetic susceptibility was measured by a SQUID magnetometer (Quantum Design,

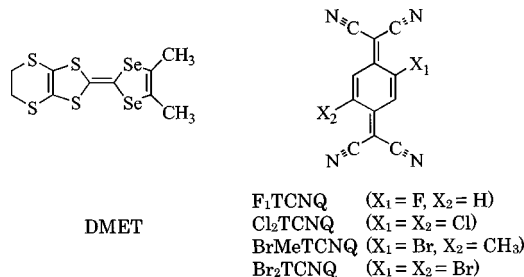


FIG. 1. Molecular structures of component donor and acceptor molecules utilized in this study.

TABLE I. Crystal data and experimental details for structural analyses of $(\text{DMET})_2(X_1X_2\text{TCNQ})$ family of complexes.

	$(\text{DMET})_2$ - (F_1TCNQ)	$(\text{DMET})_2$ - (Cl_2TCNQ)	$(\text{DMET})_2$ - (BrMeTCNQ)	$(\text{DMET})_2$ - (Br_2TCNQ)
Chem. formula	$\text{C}_{32}\text{S}_8\text{Se}_4\text{N}_4\text{H}_{23}\text{F}_1$	$\text{C}_{33}\text{S}_8\text{Se}_4\text{N}_4\text{H}_{22}\text{Cl}_2$	$\text{C}_{32}\text{S}_8\text{Se}_4\text{N}_4\text{H}_{25}\text{Br}_1$	$\text{C}_{32}\text{S}_8\text{Se}_4\text{N}_4\text{H}_{22}\text{Br}_2$
Temp.	296 K	296 K	296 K	296 K
Formula wt.	1053.12	1105.03	1129.05	1193.93
a (Å)	10.475(3)	10.595(1)	10.499(2)	10.540(2)
b (Å)	13.029(3)	13.230(2)	12.603(3)	12.637(2)
c (Å)	7.734(2)	15.578(2)	7.876(2)	7.896(19)
α (deg)	97.235(9)	69.254(4)	100.806(9)	100.630(7)
β (deg)	110.422(7)	108.194(5)	104.754(8)	104.822(7)
γ (deg)	66.954(6)	106.435(6)	99.76(1)	100.051(4)
V (Å ³)	910.2(4)	1903.1(4)	963.6(4)	971.6(3)
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Z	1	2	1	1
d (g/cm ³)	1.924	1.93	1.95	2.042
total reflcn	6764	14 041	6973	7394
Reflcn used	2578	7846	2782	2776
R, R_w	0.184, 0.370	0.061, 0.159	0.081, 0.128	0.099, 0.173
Weighting scheme	$1/\sigma^2$	$1/\sigma^2$	$1/\sigma^2$	$1/\sigma^2$
GOF ^a	5.06	2.07	1.90	2.38

^aGOF denotes goodness of fit.

MPMS-XL7) and X-band ESR spectrometer (JEOL, JES-FA 100). The electrical resistivity was measured by the four-probe method for a temperature range of 4.2–300 K.

III. CRYSTAL STRUCTURES

An isomorphous series of complexes were obtained, with the donor-to-acceptor ratio of 2:1, for four kinds of CT compounds; $(\text{DMET})_2(\text{F}_1\text{TCNQ})$, $(\text{DMET})_2(\text{Cl}_2\text{TCNQ})$, $(\text{DMET})_2(\text{BrMeTCNQ})$, and $(\text{DMET})_2(\text{Br}_2\text{TCNQ})$. All the crystallographic data are collected in Table I. Figure 2 shows the crystal structure of $(\text{DMET})_2(\text{Br}_2\text{TCNQ})$. The crystals belonged to the triclinic system, and the space group was $P\bar{1}$. In the crystals, DMET stacked to form the Q1D columns along the c axes. The strong *face-to-face* coupling of the

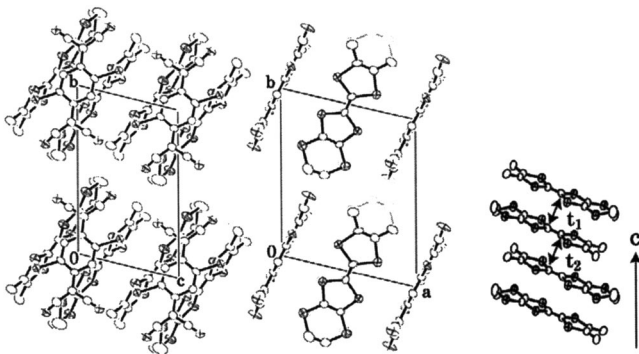


FIG. 2. Crystal structure of $(\text{DMET})_2(\text{Br}_2\text{TCNQ})$, viewed along the a axis (left), and viewed along the c axis (center), which is parallel to the donor columns whose profile is also shown in the right.

asymmetric elements of DMET molecules facilitated the strong dimerization in the stacks. These features were similar to those of $(\text{DMET})_2\text{PF}_6$ and $(\text{DMET})_2\text{AsF}_6$,¹⁰ that had been reported to exhibit spin Peierls transitions around 25 K.¹¹ The acceptor molecules contacted with the side of the DMET molecules, with the molecular planes parallel to the DMET columns. Such structural characteristic was similar to those of $(\text{TMTSF})_2(\text{Br}_2\text{TCNQ})$ (Ref. 12) and $(\text{TMTSF})_2(\text{AzaTCNQ})$ (Ref. 13).

Whereas the above features are common in the series of $(\text{DMET})_2(X_1X_2\text{TCNQ})$ being presented, a slight difference was observed in the orientations of the acceptor molecules for these complexes. In Fig. 3, we show the intermolecular arrangement of DMET dimer and adjacent TCNQ molecule for $(\text{DMET})_2(\text{Cl}_2\text{TCNQ})$ and $(\text{DMET})_2(\text{BrMeTCNQ})$, viewed along the molecular short axes of DMET's. As clearly shown, these two compounds had different features in the relative molecular orientations; long axes of TCNQ's were parallel to those of DMET's in $(\text{DMET})_2(\text{Cl}_2\text{TCNQ})$, while TCNQ long axes were at an angle of about 30° with DMET long axes in $(\text{DMET})_2(\text{BrMeTCNQ})$. Such structural features were found to be common in $(\text{DMET})_2(\text{F}_1\text{TCNQ})$ and $(\text{DMET})_2(\text{Cl}_2\text{TCNQ})$ and in $(\text{DMET})_2(\text{Br}_2\text{TCNQ})$ and $(\text{DMET})_2(\text{BrMeTCNQ})$, respectively. It implies the volume effect of large bromine substituents on the orientations of acceptor molecules. From these observations, we can firstly classify these compounds into two groups; “type I” for the former compounds and “type-II” for the latter compounds, as denoted later in the inset of Fig. 4. We note that the complexes with polar anion radicals, i.e., $(\text{DMET})_2(\text{F}_1\text{TCNQ})$ and $(\text{DMET})_2(\text{BrMeTCNQ})$, have disordered anion orientations with regard to the sub-

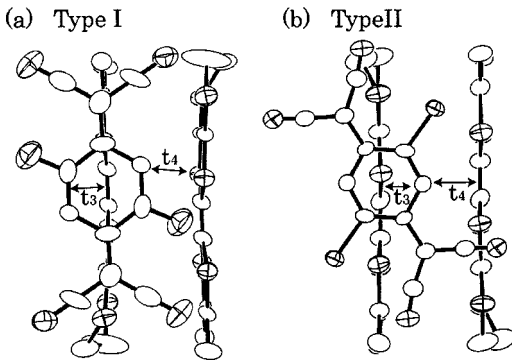


FIG. 3. Intermolecular overlap of adjacent DMET dimers and TCNQ derivative, viewed perpendicular to the donor stacks for (DMET)₂(Cl₂TCNQ) (type I) and (DMET)₂(BrMeTCNQ) (type II).

stituents, so that the type-I and type-II compounds contain one nonpolar and one polar anion, respectively.

We calculated intermolecular transfer integrals by means of extended Hückel molecular orbital method.¹⁴ The result is shown in Table II. Here, *t*₁ and *t*₂ are transfer integrals between DMET molecules as denoted in the right side of Fig. 2, while *t*₃ and *t*₄ are transfer integrals between DMET and TCNQ molecules as schematically shown in Fig. 3. All the complexes had almost similar values for the intra- and inter-dimer interactions, which were amounted to be in the range of 120–150 meV and 60–80 meV, respectively. This result demonstrates the rather strong dimerization in the DMET-based donor stacks for these complexes. In contrast, intermolecular interactions between donors and acceptors were in the range of 5–25 meV along the *a* axes, indicating the strong one-dimensionality of donor columns as well as the localized nature of TCNQ anion radicals. From the C≡N stretching mode of vibrational spectra, we found that TCNQ derivatives were fully ionized in all the isomorphous complexes. From the result, it is clear that the series of (DMET)₂(X₁X₂TCNQ) complexes commonly had DMET-based 1/4-filling Q1D donor stacks (DMET = +1/2) with in-

TABLE II. Intermolecular transfer integrals (meV) for various combinations of neighboring molecules in (DMET)₂(X₁X₂TCNQ) family of complexes.

Complex	(DMET) ₂ ⁻ (F ₁ TCNQ)	(DMET) ₂ ⁻ (Cl ₂ TCNQ)	(DMET) ₂ ⁻ (BrMeTCNQ)	(DMET) ₂ ⁻ (Br ₂ TCNQ)
<i>t</i> ₁	127	147	126	121
<i>t</i> ₂	61.5	63.2	76.1	71.3
<i>t</i> ₃	22.5	25.2	22.4	24.2
<i>t</i> ₄	6.3	4.1	11.8	11.3

herent 4k_F periodicity. We note that only in (DMET)₂(Cl₂TCNQ), the cell unit along the stacking axes was doubled, where each unit cell contained two dimers at room temperature. It also indicates that the 2k_F-type lattice distortions were already appeared at room temperature in (DMET)₂(Cl₂TCNQ).

Room temperature electrical conductivity was obtained as 0.1–1 S/cm for all the complexes along the *c* axes. The conductivity exhibited semiconducting behaviors in the whole measured temperature range, whose activation energies were estimated as in the range of 5–50 meV for these complexes. This behavior can be primarily associated with charge gaps in the donor stacks, in which the intradimer Coulomb interaction may split the conduction band of DMET stacks into the lower and upper Hubbard bands. It is interesting to point out that (TMTSF)₂(Br₂TCNQ) and (TMTSF)₂(AzaTCNQ), both of which had similar crystal structures with (DMET)₂(X₁X₂TCNQ), showed higher electrical conductivity of about 100 S/cm at room temperature. The comparatively lower electrical conductivity in (DMET)₂(X₁X₂TCNQ) is likely to be associated with the lower symmetry of DMET molecules, which should lead to the strong dimerization in the donor stacks.

IV. MAGNETIC PROPERTIES

Figure 4 shows temperature dependence of static magnetic susceptibility in four kinds of (DMET)₂(X₁X₂TCNQ). The susceptibilities exhibited Curie-Weiss-like enhancement with decrease of the temperature for all the complexes above about 10 K. The susceptibility kept increasing in (DMET)₂(F₁TCNQ) and (DMET)₂(Cl₂TCNQ) down to the lowest temperature of 2 K, while sharp drops were observed for (DMET)₂(BrMeTCNQ) and (DMET)₂(Br₂TCNQ) around 7 K and 5 K, respectively. From these observations, it was found that the difference in the orientation of acceptor molecules was clearly reflected in the magnetic properties of these compounds. Analyses of Curie-Weiss-like enhancement above 10 K suggested the existence of about one localized spin per formula unit for all the above complexes, in spite of the existence of two paramagnetic spin components: dimer spin of (DMET)₂⁺ and anion radical spin of TCNQ⁻.

To investigate the roles of the respective spin states, we measured EPR spectra on their single crystals at various temperatures. In all the measured range, we observed single Lorentzian features in the EPR spectra, which can be ascribed to the contribution of both spin components averaged

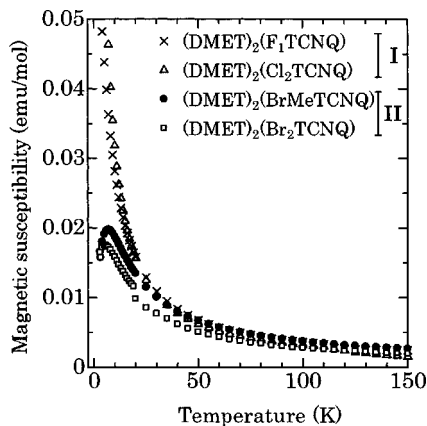


FIG. 4. Temperature dependence of static magnetic susceptibility for (DMET)₂(F₁TCNQ) (×) and (DMET)₂(Cl₂TCNQ) (Δ) (type I), and (DMET)₂(BrMeTCNQ) (●) and (DMET)₂(Br₂TCNQ) (□) (type II).

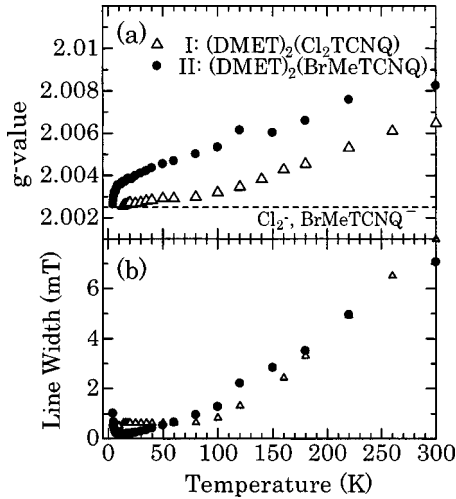


FIG. 5. Temperature dependence of EPR (a) spin susceptibility χ_{spin} , (b) g value, and (c) line width of (DMET)₂(Cl₂TCNQ) (Δ), and (DMET)₂(BrMeTCNQ) (\bullet). The g value is clearly different between these compounds.

by the exchange-narrowing effect. We found that the spin susceptibility that was obtained by integrating the EPR signals was consistent with the results shown in Fig. 4. Temperature dependences of g values and the linewidths are shown in Fig. 5(a) and 5(b), respectively, for (DMET)₂(Cl₂TCNQ) [type I] and (DMET)₂(BrMeTCNQ) [type II]. As seen in this plot, the g values decreased with decreasing temperature in both complexes. However, we also notice that the g value of (DMET)₂(BrMeTCNQ) [type II] was quite larger than that of (DMET)₂(Cl₂TCNQ) [type I], and exhibited a sharp drop below 7 K. In (DMET)₂(BrMeTCNQ), the linewidth also showed appreciable jump below 7 K. These observations imply the occurrence of the second-order phase transition at 7 K in the spin systems of (DMET)₂(BrMeTCNQ). In Fig. 5(a), we also show the g values of Cl₂TCNQ⁻¹ and BrMeTCNQ⁻¹ by a dashed line. From this plot, it is evident that the contribution of the anion radicals in both of the complexes became dominated in the magnetic properties, with approaching the lowest temperature. Here it is noted that the g values of (DMET)₂(F₁TCNQ) and (DMET)₂(Br₂TCNQ) were found to be almost coincident with those of (DMET)₂(Cl₂TCNQ) and (DMET)₂(BrMeTCNQ), respectively, at room temperature.

On the basis of the obtained g values, we extracted the contribution of each spin components in the observed magnetic susceptibility. In Fig. 6, we show the temperature dependence of each spin components; χ_{DMET} (filled circles) χ_{TCNQ} (open circles) in (DMET)₂(BrMeTCNQ). From this plot, it is clear that the observed sharp drop in the static susceptibility of (DMET)₂(BrMeTCNQ) should be associated with the magnetic transition in the DMET stacks. Considering that the decrease in the static susceptibility was also clearly observed below 7 K, this observation is most likely associated with the spin-Peierls transition, rather than with the antiferromagnetic transition, of the donor stacks in (DMET)₂(BrMeTCNQ). In contrast, the χ_{DMET} of

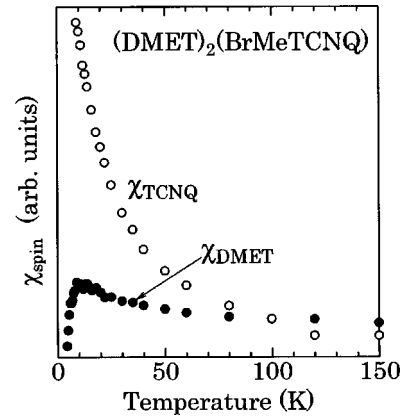


FIG. 6. Individual contributions of spin susceptibility in (DMET)₂(BrMeTCNQ) from the DMET stacks (χ_{DMET}) plotted by filled circles and TCNQ sites (χ_{TCNQ}) by open circles.

(DMET)₂(Cl₂TCNQ) was much smaller in all the measured range than that of (DMET)₂(BrMeTCNQ), as seen in the comparative lower g values in (DMET)₂(Cl₂TCNQ). It clearly indicates the existence of a magnetic gap in the DMET stacks of (DMET)₂(Cl₂TCNQ) at higher temperature. This feature is also consistent with the $2k_F$ -type periodicity in the crystal structures as was presented before. We also note that superlattice reflections associated with the $2k_F$ -type lattice distortions were also observed in (DMET)₂(F₁TCNQ) below 250 K. All the above experimental observations led us to conclude that the type-I compounds exhibited the $2k_F$ transitions at relatively higher temperature (at least more than 250 K), while the type-II compounds at low temperature below 7 K. In both types of the complexes, the Curie-Weiss-like magnetic properties in the acceptor site did not seem to be affected by the $2k_F$ -type lattice distortions in the DMET stacks.

V. $2k_F$ INSTABILITIES IN (DMET)₂(X₁X₂TCNQ)

From the above experimental results it was found that the isomorphous 1/4-filling molecular stacks undergo considerably different $2k_F$ lattice (BOW) transitions, as triggered by a subtle change in the orientations of subsidiary acceptor molecules. Considering that the structural features of the DMET stacks are almost similar with each other, as evidenced by the intermolecular interactions shown in Table II, such a difference in the $2k_F$ transition temperatures should be originated in the environmental aspects of the DMET stacks. The following mechanism can be considered as the origin of such differences; dimensionality as mediated by the intermolecular interaction with acceptor molecules, variation in the phonon energy invoked by the van der Waals interaction with acceptor molecules, or change in the electrostatic interactions by the anion radicals.

It is known that the $2k_F$ transitions in 1/4-filling molecular stacks assumed intermediate character between the regular Peierls and spin Peierls transitions,¹⁵ where the charge and spin degrees of freedom more or less contributed depending on the U_{dimer} and $t_{\text{interdimer}}$ values and also on the transition temperatures.¹⁶ Considering that there is more en-

ergy associated with electron transfer $t_{\text{interdimer}}$ than spin exchange $J = (t_{\text{interdimer}})^2 / U_{\text{dimer}}$, the charge degrees of freedom might be more strongly associated with the $2k_F$ transitions in the type-I compounds, as seen from the relatively high electrical conductivity with low activation energy and high transition temperatures. On the other hand, the $2k_F$ transitions are suppressed at room temperature in the type-II compounds, where the suppression might be further enhanced by the stabilization of Mott-Hubbard charge gap down to low temperature; as the temperature lowered, charge gap becomes stabilized that should suppress the BOW formation associated with the Peierls mechanisms. Nonetheless, at very low temperature, the spin Peierls instability dominated and finally led to the $2k_F$ transition. In such a case, the $2k_F$ instability may assume the more spin-Peierls character, as was found from the extremely high electrical resistivity ($> 1 \text{ T}\Omega \text{ cm}$) at the transition temperature. It means that the (DMET)₂(X₁X₂TCNQ) system provides the series of 1/4-filling Q1D compounds that are located in the vicinity of a border between purely spin-Peierls and generalized $2k_F$ transitions. However, one-dimensionality might not be a crucial factor in the difference in the $2k_F$ transition temperatures, since the one-dimensionality is more effective in type II compounds with larger substituents in contradiction to the observation.

One of the driving mechanisms of the above difference, the change in the electrostatic interactions by the anion radicals can be considered. Since the negative charge is mainly located on the end nitrogen atoms in the TCNQ molecules,¹⁷ the change in the molecular orientations of the acceptor molecules should lead to the modulation of $4k_F$ potential on the DMET molecular stacks. This feature might provide the

charge disproportionation in the Q1D molecular stacks at room temperature, while the central symmetry is preserved in the electrostatic modulations both in the type-I and type-II compounds. In recent theoretical studies it has been discussed that the $2k_F$ lattice modulations are always accompanied by charge-density modulations (CDW's) of weaker amplitudes, where a strong enough short-range electronic repulsion plays important roles in the $2k_F$ and $4k_F$ charge modulations.^{4,5,18} The series of the compounds being presented could provide a unique system to investigate the interplay between electronic correlation and lattice effects in the 1/4-filling Q1D molecular stacks that have been addressed in a number of recent theoretical studies. The next challenge is to elucidate the role of the charge disproportionation in the $2k_F$ instabilities of the molecular stacks.

VI. SUMMARY

In summary, we obtained an isomorphous series of 1/4-filling Q1D organic semiconductors, (DMET)₂(X₁X₂TCNQ), which exhibits $2k_F$ transitions, ranging from 6 K to higher than 300 K. We found that a slight change in the orientations of subsidiary anion radicals triggered a considerable change from the regular Peierls to the spin Peierls transitions in the 1/4-filling Q1D Mott-Hubbard-type organic semiconductors.

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