Crystal Structure of an Ionic Charge-Transfer Complex of DAP–F_4TCNQ (DAP = 1,6-Diaminopyrene, F_4TCNQ = 2,3,5,6-Tetrafluoro-7,7,8,8-tetracyano-*p*-quinodimethane)

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A charge-transfer complex of DAP with F_4TCNQ has been obtained by electrochemical reduction of F_4TCNQ in acetonitrile in the presence of DAP·BF_4. The crystal comprises segregated one-dimensional columns of donors and acceptors with CH_3CN as the crystal solvent. The molecular geometry and infrared spectrum show that the donor and acceptor components are completely ionized. These features are the same as those found in DAP·TCNQ. However, a marked difference lies in the column structure; both the DAP and F_4TCNQ columns are composed of the dimerized units, while they are uniform in DAP·TCNQ. The difference can be accounted by the increase of the transfer energy in DAP·F_4TCNQ·CH_3CN compared with DAP·TCNQ.

The ground states of charge-transfer complexes, which can be evaluated from the donor and acceptor strengths,[1] dominate their physical properties. When a strong donor is combined with a relatively strong acceptor, a complex with an ionic ground state will be obtained. In such a case, the component molecules may crystallize into two different structures: mixed-stack structure or segregated-stack structure. DAP·TCNQ is one of the latter examples.[2] The component molecules are almost completely ionized. DAP and TCNQ each form a one-dimensional column in which the interplanar spacing is uniform. In this complex, the on-site Coulomb repulsion energy (U) has been suggested to play an important role, and the DAP·TCNQ crystal may, therefore, be categorized as a kind of Mott–Hubbard insulator. However, its electrical resistivity at room temperature is relatively low for such an insulator, ca. 10^{-1} Ω cm at room temperature. Interestingly, the activation energy of the conduction is unexpectedly large for a material with such a high conductivity, 0.26 eV; the value is rather close to that expected for an insulator. In order to clarify this contradiction, high conductivity with large activation energy, its more detailed physical properties have been studied.[3] The optical and magnetic studies have suggested that the dimerization grows locally along the chain with decreasing temperature, though no clear long-range lattice deformation has been observed down to 118 K by X-ray diffraction.[2] DAP·TCNQ may be regarded as a spin-Peierls system, in which the electronic origin (electron–electron correlation) competes with the magnetic origin (J (magnetic exchange coupling) $\propto t^2$; t = transfer energy). The hydrogen bonds formed between DAP and TCNQ have some relation to the amplitude of the dimerization.[3] However, this point has not been clarified yet, since there are no other structurally characterized members in the DAP·TCNQ family.

We have thus intended to characterize the crystal structures of the DAP·TCNQ family systematically. Among the family, one of the strong acceptors, F_4TCNQ, has been found to form a crystalline charge-transfer complex when the reaction is performed electrochemically in acetonitrile using DAP·BF_4 as the electrolyte. In this paper, we describe its crystal structure and compare it with that of DAP·TCNQ.

Experimental

Materials. DAP was synthesized and purified by a reported method.[4,5] DAP·BF_4 was synthesized as follows. DAP and NO·BF_4 were weighed (each 1 mmol) and transferred into a flask equipped with a gas inlet in a glove box under a nitrogen atmosphere. Degassed dichloromethane was transferred into the flask at 77 K by a bulb-to-bulb method. The solidified mixture was then warmed up to room temperature with stirring under a nitrogen atmosphere. NO gas evolution was observed during the warming and the black powder of DAP·BF_4 was formed. The solid product was collected by filtration and washed with diethyl ether (yield 79%). F_4TCNQ was commercially purchased and was used without further purification. Single crystals of the F_4TCNQ complex were grown by the electrochemical reduction of F_4TCNQ in acetonitrile with DAP·BF_4 as the electrolyte. The crystals were unstable in open air, and were found to contain the crystal solvent. The composition of DAP·F_4TCNQ·CH_3CN has been confirmed by the X-ray structure analysis results.

X-Ray Structure Analysis. An automated Rigaku AFC-7R diffractometer with graphite-monochromated Mo $K\alpha$ radiation (λ = 0.71073 Å) was used for data collection at 296 K. Since the crystal contains crystal solvents and is unstable, it was sealed in a glass capillary with a small amount of the solution in the electrochemical cell. The data were corrected for Lorentz and polarization effects. Three standard reflections monitored every 150 data measurements showed the deviations to be less than 2.5% in F, and so no decay correction was applied. The data-collection conditions and crystal data are summarized in Table 1. The crystal

Table 1. Data-Collection Conditions and Crystal Data of DAP·F_4TCNQ·CH_3CN

Chemical formula	$C_{30}H_{15}F_4N_7$
Molecular weight	549.49
Crystal size/mm	$0.10 \times 0.03 \times 0.80$
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	13.293(4)
b/Å	15.600(4)
c/Å	6.744(2)
α/°	94.27(2)
β/°	103.93(3)
γ/°	70.00(2)
V/Å^3	1275.3(6)
Z	2
D_{calc}/g cm^{-3}	1.431
μ(Mo $K\alpha$)/cm^{-1}	1.09
2θ range	$5° < 2\theta < 55°$
Scan width/degrees	$1.42+0.30 \tan\theta$
Scan mode	$\omega - 2\theta$
Scan rate/degrees min^{-1}	16
No. of reflections measured	5879
No. of independent reflections observed [$I > 1.40\sigma(I)$]	1687
No. of parameters	355
R	0.079
R_w	0.046

structure was solved by a direct method (SIR 92[6]), and the positions of the hydrogen atoms, except for those included in CH_3CN, were placed at the calculated ideal positions. A full-matrix least-squares technique (teXsan[7]) with anisotropic thermal parameters for non-hydrogen atoms of DAP and F_4TCNQ and isotropic for non-hydrogen atoms of the crystal solvent and hydrogen atoms of DAP (1.2 times of the attached carbon or nitrogen) was employed for a structure refinement.[8]

Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition numbers CCDC 147074.

Results and Discussion

Molecular and Crystal Structure of DAP·F_4TCNQ·CH_3CN. The independent molecular units in the unit cell are shown in Fig. 1, and the atomic parameters are listed in Table 2. Since DAP is a strong donor (the redox potential for the first oxidation, E_{ox} = 0.24 V vs. Ag/AgCl in acetonitrile) and F_4TCNQ is a strong acceptor (the potential for the first reduction, E_{red} = 0.54 V), the complex is expected to have an ionic ground state.[1] Since the molecular geometry change due to the formal charge on the molecule has not been determined precisely for F_4TCNQ, the geometry of DAP has been examined. The C–N bond length in DAP was recognized as being sensitive to the formal charge.[9] The averaged C–N bond length of DAP in DAP·F_4TCNQ·CH_3CN is 1.345(10) Å and is quite close to that of $DAP^{+\bullet}$ (1.387(2) Å for DAP^0 and 1.334(2) Å for $DAP^{+\bullet}$). Since the crystal available for the diffraction study was rather thin, the standard deviation values are relatively large. Due to this fact the final quantitative estimation was made by the optical measurement as described below.

The formal charge on the molecule can also be estimated from the vibrational spectra. This information is available for F_4TCNQ,[10] and the data are compiled in Table 3. From this comparison, it can be clearly seen that F_4TCNQ in DAP·F_4TCNQ·CH_3CN is completely ionic.

The crystal structure is shown in Fig. 2. DAP and F_4TCNQ each form a one-dimensional column along the c-axis. As can be expected from the dimension of the c-axis, 6.744(2) Å, the one-dimensional columns contain dimerized deformation. The alternation of the interplanar spacing is more significant in the DAP column (3.260 and 3.472 Å) than in the F_4TCNQ column (3.238 and 3.245 Å). Two overlap modes for each column are shown in Fig. 3. Two overlap modes between the DAP cations are nearly the same, and the shifting direction is alternately changed. These overlap modes are slightly

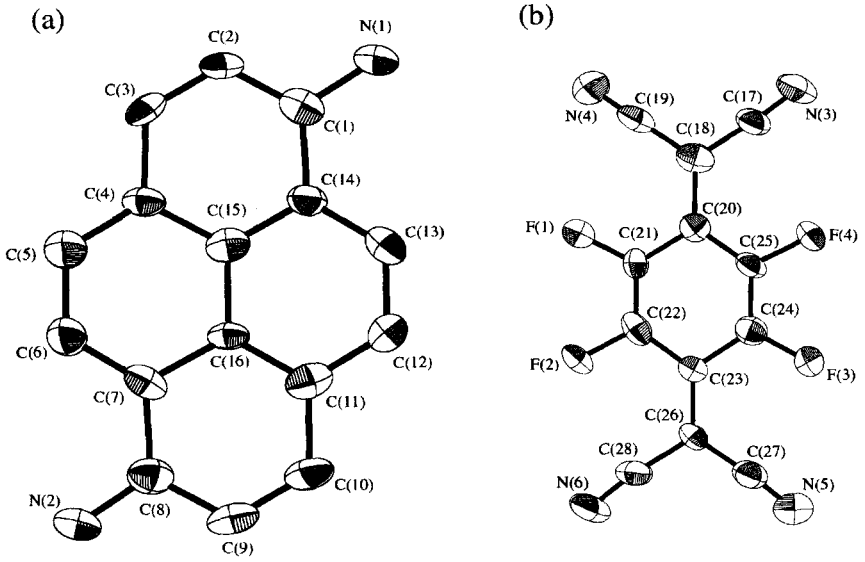

Fig. 1. ORTEP drawing of DAP (a) and F_4TCNQ (b) in DAP·F_4TCNQ·CH_3CN showing the atom numbering scheme.

Table 2. Fractional Coordinates and Equivalent Temperature Factors for DAP·F_4TCNQ·CH_3CN

Atom	x	y	z	B_{eq}/Å^2
N(1)	0.5458(6)	0.2317(5)	0.296(1)	4.1(2)
N(2)	0.3774(6)	−0.2526(5)	0.202(1)	4.6(3)
C(1)	0.5673(8)	0.1410(6)	0.300(1)	3.1(3)
C(2)	0.6741(7)	0.0826(6)	0.354(1)	3.1(3)
C(3)	0.6999(7)	−0.0084(6)	0.356(1)	3.3(3)
C(4)	0.6167(7)	−0.0504(6)	0.311(1)	2.6(2)
C(5)	0.6411(7)	−0.1459(6)	0.314(1)	3.4(3)
C(6)	0.5592(7)	−0.1827(6)	0.274(1)	3.4(3)
C(7)	0.4491(8)	−0.1272(6)	0.228(1)	2.8(3)
C(8)	0.3583(7)	−0.1631(6)	0.187(1)	3.4(3)
C(9)	0.2481(7)	−0.1032(7)	0.128(1)	3.8(3)
C(10)	0.2235(7)	−0.0119(7)	0.113(1)	3.9(3)
C(11)	0.3089(7)	0.0285(7)	0.163(1)	3.3(3)
C(12)	0.2852(7)	0.1234(6)	0.153(1)	3.4(3)
C(13)	0.3676(7)	0.1599(6)	0.198(1)	3.5(3)
C(14)	0.4771(7)	0.1054(6)	0.250(1)	2.8(3)
C(15)	0.5046(7)	0.0100(7)	0.259(1)	2.6(3)
C(16)	0.4199(7)	−0.0290(6)	0.214(1)	2.3(2)
F(1)	1.1452(4)	0.3400(4)	0.8469(9)	4.7(2)
F(2)	0.9618(4)	0.3172(3)	0.6502(9)	4.8(2)
F(3)	0.7915(4)	0.6372(4)	0.5690(9)	4.8(2)
F(4)	0.9743(4)	0.6606(4)	0.7652(9)	4.7(2)
N(3)	1.1959(7)	0.6674(6)	1.023(1)	4.9(3)
N(4)	1.3481(7)	0.3826(6)	1.075(1)	5.8(3)
N(5)	0.5830(7)	0.5913(6)	0.373(1)	5.8(3)
N(6)	0.7341(7)	0.3097(6)	0.420(1)	5.7(3)
C(17)	1.1806(8)	0.6014(7)	0.972(2)	3.7(3)
C(18)	1.1723(8)	0.5142(7)	0.923(1)	3.5(3)
C(19)	1.2704(8)	0.4396(8)	1.006(2)	3.8(3)
C(20)	1.0705(7)	0.5020(6)	0.817(1)	2.8(3)
C(21)	1.0593(8)	0.4143(7)	0.783(2)	3.2(3)
C(22)	0.9626(8)	0.4042(6)	0.680(1)	3.3(3)
C(23)	0.8640(7)	0.4753(6)	0.600(1)	2.6(3)
C(24)	0.8777(8)	0.5620(7)	0.640(2)	3.2(3)
C(25)	0.9744(7)	0.5730(7)	0.742(1)	3.1(3)
C(26)	0.7646(7)	0.4644(6)	0.495(1)	3.2(3)
C(27)	0.6656(8)	0.5364(7)	0.430(2)	3.8(3)
C(28)	0.7533(7)	0.3762(7)	0.456(2)	3.7(3)
N(7)	0.9915(7)	0.0948(6)	0.716(1)	7.6(3)
C(29)	0.9701(8)	0.1416(7)	0.335(2)	6.1(3)
C(30)	0.9809(9)	0.1164(7)	0.541(2)	6.3(3)

Table 3. Frequency of the Vibrational Modes of F_4TCNQ (cm^{-1})

Mode	F_4TCNQ^0	$F_4TCNQ^{-a)}$	DAP·F_4TCNQ·CH_3CN
$b_{1u}\nu_{19}$	1549	1500	1498
$b_{2u}\nu_{33}$	1602	1539	1540

a) Ref. 10.

different from that observed for DAP·TCNQ in which a ring-over-bond type overlap of DAP is achieved by an additional shift along the transverse direction. However, this difference does not affect the overlap integral value (vide infra). On the other hand, the dimerization effect is more pronounced in the overlap modes between the F_4TCNQ anions. The overlap (iii) in Fig. 3 is nearly eclipsed, while the overlap (iv) is an ordinary ring-over-bond type. The overlap integrals also

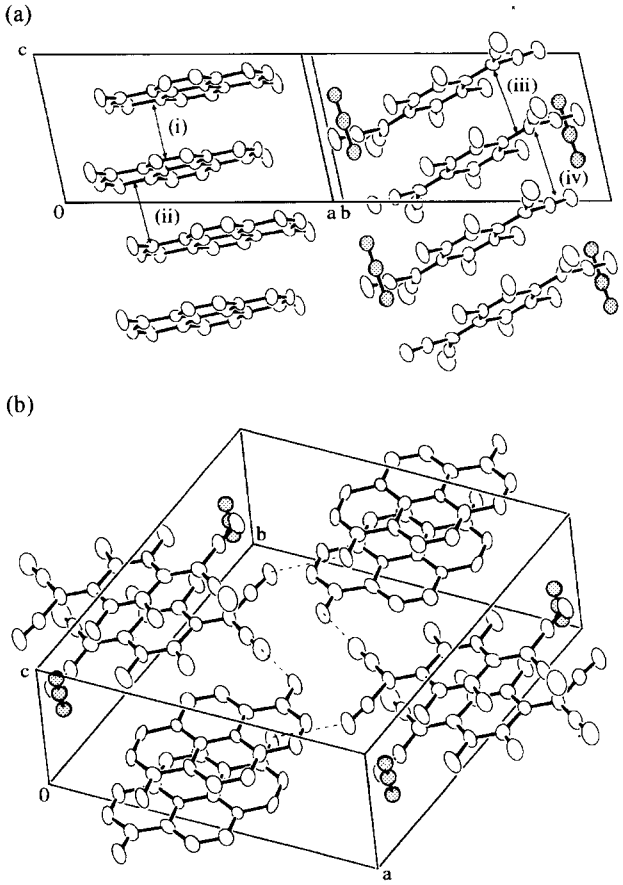

Fig. 2. The crystal structure of DAP·F_4TCNQ·CH_3CN; its columnar structure (interplanar spacing; 3.260 Å (i), 3.472 Å (ii), 3.245 Å (iii), and 3.238 Å (iv)) (a) and the hydrogen-bonding network (b). Shaded molecules are CH_3CN.

reflect this difference as discussed later.

Between the DAP and F_4TCNQ columns, the N–H···N hydrogen bonds exist. The N···N distances are in the range of 3.01—3.06 Å, and they are considered to be intermediate strength hydrogen-bonds.[11] The hydrogen-bonding network is formed parallel to the (1 0 $\bar{1}$) plane. The CH_3CN molecules occupy an open channel along the c-axis formed between the columns, and have no specific interactions with DAP or F_4TCNQ. Therefore, the crystal solvents may be easily removed from the open channel, which may be the reason why the crystal is so unstable. This instability makes it extremely difficult for us to measure its single-crystal physical properties. The electrical conductivity of the mosaic crystal was 10^{-3}—10^{-2} S cm^{-1} at room temperature, with semiconducting behavior (activation energy; 0.17 eV). This observation is consistent with its dimerized structure, though the conductivity value also contains the resistance at the domain boundaries.

Comparison between DAP·TCNQ and DAP·F_4TCNQ·CH_3CN. Both of these complexes have ionic ground states. The segregated one-dimensional column structure is also in common. The most significant difference is that the dimerization deformation (Peierls distortion) occurs in DAP·F_4TCNQ·CH_3CN, while uniform columns are formed

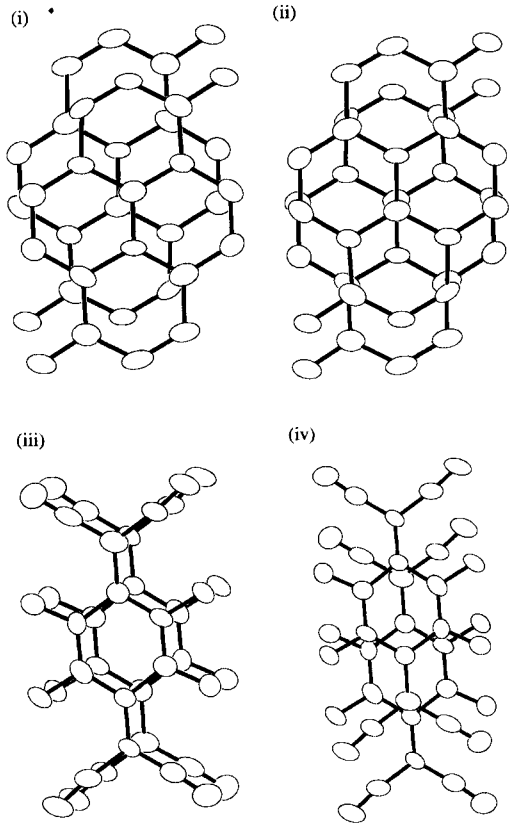

Fig. 3. Molecular overlaps in DAP·F_4TCNQ·CH_3CN. The notations are the same as shown in Fig. 2.

in DAP·TCNQ. Therefore, DAP·TCNQ is assumed to be a Mott-type insulator and DAP·F_4TCNQ·CH_3CN is assumed to be a Peierls-type insulator. This is rather interesting since the on-site Coulomb repulsion energy of TCNQ is not so much different from that of F_4TCNQ.[12] Then, we have examined the transfer energy between the overlapped molecules. The overlap integral values between the frontier orbitals obtained from an extended Hückel calculation based on the structural data are shown in Fig. 4. The dimerization deformation effect is more significant in the F_4TCNQ column than in the DAP column in terms of the electronic structure as found in the overlap modes, though it is reversed in terms of the interplanar distance. In both complexes, the predominant values are obtained in the acceptor columns. The values between the DAP molecules are rather small and do not change significantly between the TCNQ complex and the F_4TCNQ complex: 13.9×10^{-3} for the TCNQ complex and 14.1×10^{-3} (averaged) for the F_4TCNQ complex. On the other hand, the value between the acceptor molecules is much larger in the F_4TCNQ complex than in the TCNQ complex: 16.5×10^{-3} for TCNQ and 20.5×10^{-3} (averaged) for F_4TCNQ. Since these complexes have one-dimensional electronic systems, the increase of transfer energy is considered to be the origin of the switching from the Mott-type insulator to the Peierls-type insulator. Indeed, the value for F_4TCNQ is still larger than that for TCNQ at 118 K, 18.7×10^{-3}, at which temperature no long-range order lattice deformation was observed.[2]

Though the transfer energy change in the acceptor columns is assumed as the origin of the structural difference, the roles of the hydrogen bonds and crystal solvents are still an open question. The strength of the hydrogen bonds in DAP·TCNQ is nearly the same as that in DAP·F_4TCNQ·CH_3CN; the N···N distances are 2.980(2) and 3.020(2) Å in the former and are 3.01(1), 3.01(1), 3.05(1), and 3.06(1) Å in the latter. From the structural study on the F_4TCNQ complex, an interesting feature of the relationship between the lattice dimerization and the hydrogen-bonding network has been found. As schematically shown in Fig. 5, each DAP molecule in a dimerized pair is connected by hydrogen bonds with the F_4TCNQ molecules belonging to different pairs, and vice versa. Therefore, the hydrogen-bonding force seems to operate against the lattice dimerization. In the F_4TCNQ complex, the electronic energy gain by the dimerization must surpass not only the on-site Coulomb repulsion energy but also the strain due to the hydrogen-bonding force. It is not clear whether the relationship between the dimerization lattice deformation and the hydrogen-bonding network is in common for this type of hydrogen-bonding charge-transfer complexes or not. If this relationship can be applied to the TCNQ complex, the hydrogen-bonds between the DAP and

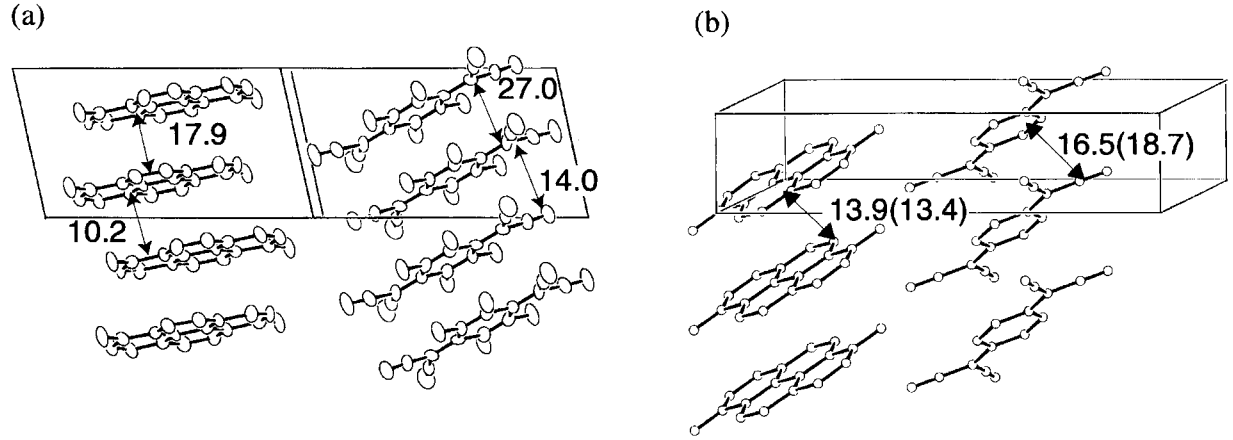

Fig. 4. Absolute overlap integral values ($\times10^3$) in DAP·F_4TCNQ·CH_3CN (a) and in DAP·TCNQ (b). The values in parentheses in (b) are those at 118 K.

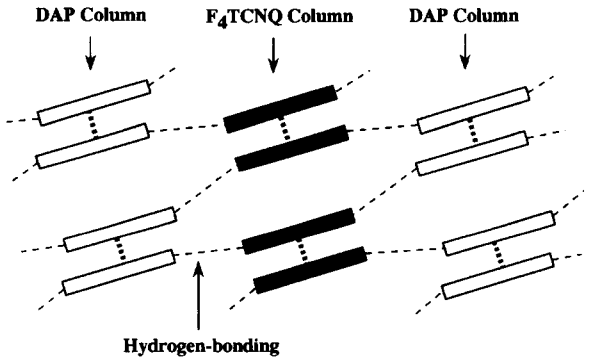

Fig. 5. Schematic drawing of the hydrogen-bonding network and the lattice dimerization in DAP·F_4TCNQ·CH_3CN.

TCNQ columns may operate to suppress the lattice dimerization, which will cause the absence of the long-range ordering of the lattice dimerization in DAP·TCNQ.

In conclusion, an ionic charge-transfer complex, DAP·F_4TCNQ·CH_3CN, has been prepared by an electrochemical method, and has been structurally characterized. Dimerization in the segregated one-dimensional column structure is observed. This situation contrasts to DAP·TCNQ in which the molecules are uniformly stacked. The difference arises from the increase of the transfer energy in DAP·F_4TCNQ·CH_3CN compared with DAP·TCNQ. If one can assume that t (transfer energy in eV) = $-10\times S$ (S = overlap integral),[13] the $4|t|$ value (band width) of the F_4TCNQ column is 0.82 eV and that of the TCNQ column is 0.66 eV at 296 K and 0.75 eV at 118 K. This relatively small difference suggests that both complexes situate near the boundary between the Peierls-type insulator and the Mott-type insulator.

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