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NEUTRAL-IONIC TRANSITION OF CHARGE TRANSFER COMPLEXES OF TTF AND TETRAHALO-*p*-BENZOQUINONES

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Abstract Pressure-induced neutral-ionic (N-I) transition was observed in new charge transfer complexes of TTF and tetrahalo-*p*-benzoquinones, *i. e.*, a 1:1 complex and three 2:1 complexes. The transition in the 2:1 complexes was different from that in $(TTF)_2IA$ previously reported, where IA is *p*-iodanil. Two acceptor sites of different ionicities were observed in the former above the transition pressure (2.0 GPa), although $(TTF)_2IA$ showed only one acceptor site. Two C–S stretching IR peaks corresponding to different ionicities of TTF sites appeared in the ionic phase. The appearance shows asymmetric charge distribution over the two TTF moieties of the trimer unit, TTF-quinone-TTF. These results suggest that a couple of trimers behave cooperatively in the N-I transition.

Keywords: Pressure dependence, IR spectra, diamond anvil cell, crystal structure, asymmetric charge distribution

INTRODUCTION

Organic charge transfer (CT) complexes of 1:1 composition have either segregated column where donors (D) and acceptors (A) form columns separately or mixed column where D and A molecules mutually stack. Degree of ionicity (γ) of D and A sites is determined by a balance between energy gain by the electrostatic Madelung energy (E_M) in an ionic crystal lattice and energy cost on ionization of a donor-acceptor pair ($I_D - E_A$) in a neutral crystal lattice, where I_D is the ionization potential of D and E_A is the electron affinity of A. Ionicity ranging from quasi-neutral ($\gamma \approx 0$)[1] to quasi-ionic ($\gamma \approx 1$)[2] is observed in complexes with the mixed column. On the other hand, the segregated column is not stable in the neutral state because no CT force works between neutral D and D or neutral A and A. In the case of complexes of tetrathiafulvalene

(TTF) and tetrahalo-*p*-benzoquinones, which have the mixed column, I_D–E_A and E_M have comparable magnitudes with one another.[3] Hence, molecular packing in the crystal plays an important role in determinig γ of the complex.

The neutral-ionic (N-I) transition has been found first in a neutral CT complex, TTF-CA,[4] where CA is *p*-chloranil (tetrachloro-*p*-benzoquinone). The N-I transition of TTF-CA has been investigated in detail,[5-8] while other CT complexes[9] have never been fully investigated to our knowlege. We have searched various CT systems showing N-I transition to elucidate the mechanism of the transition. We found N-I transition in two CT complexes of 1:1 composition, TTF-IA[10] and TTF-DMDCNQI,[1] where IA is *p*-iodanil (tetraiodo-*p*-benzoquinone) and DMDCNQI is 2,5-dimethyldicyanoquinonediimine. In TTF-IA, a small ionicity jump of 0.1 was observed, which is attributable to the large polarizability of IA molecules. In TTF-DMDCNQI, on the other hand, a large ionicity jump of 0.8 is the characteristic feature of the N-I transition, which is caused by small transfer integral between TTF and DMDCNQI. These new CT crystals gave model systems other than TTF-CA for theoretical calculations of the N-I transition in CT crystals of 1:1 composition.[11]

Recently, we found pressure-induced N-I transition in $(TTF)_2IA$.[12] It is important that N-I transition has been found in a complex of 2:1 composition, because the systems showing the N-I transition have so far been complexes of 1:1 composition without exception. X-ray structure analysis[13] showed that at ambient pressure the crystal of $(TTF)_2IA$ was composed of symmetric trimer units, TTF-IA-TTF, which are independent of each other. The N-I transition of this complex was found from the pressure dependence of the C=O stretching IR frequency of IA.[12] The frequency indicated that γ of IA gradually increased with pressure and discontinuously changed from 0.46 to 0.54 at 3.1 GPa and then finally increased to 0.64 at 6.3 GPa. Ionicity of the TTF sites can be estimated from C–S stretching frequencies of TTF.[10,12] In this case, IR peaks assigned to neutral and ionic TTF species were simultaneously observed above the transition point. This result suggests nonuniform charge distribution between the two TTF moieties of the trimer unit.[14] This is a characteristic feature of the N-I transition in 2:1 CT complexes distinguished from that in TTF-CA. Other examples are necessary to elucidate the nature of the N-I transition. Here we report N-I transitions of three 2:1 CT complexes together with a complex of 1:1 composition.

EXPERIMENTAL

2-Bromo-3,5,6-trichloro-*p*-benzoquinone (TCLQ),[15] 2,5-Dibromo-3,6-dichloro-*p*-benzoquinone (25BRQ)[16] and 2,3,5-Tribromo-6-chloro-*p*-benzoquinone (TBRQ)[17] were synthesized from trichlorohydroquinone, 2,5-dichloro-*p*-benzoquinone and chlorohydroquinone, respectively, by reaction with bromine in acetic acid. 2,3-Dibromo-5,6-dichloro-*p*-benzoquinone (23BRQ) was kindly given by another laboratory. All the quinones were purified by recrystalization from toluene followed by sublimation *in vacuo*. The quinones were identified by elemental analyses and IR spectra. TTF purchased from Tokyo Kasei Co. was purified by sublimation *in vacuo*.

Charge transfer complexes were prepared by mixing hot acetonitrile solutions of each component molecule in 1:1 stoichiometry. After cooling the solutions, we obtained four solid complexes as single crystals: TTF-TCLQ, $(TTF)_2$25BRQ, $(TTF)_2$23BRQ, $(TTF)_2$TBRQ. Compositions of the complexes were determined by elemental analyses and X-ray crystal structure analyses except for $(TTF)_2$23BRQ. Anal. Calc. for $C_{12}H_4O_2S_4Cl_3Br$: C, 29.1; H, 0.8. Found: C, 29.5; H, 0.81. Anal. Calc. for $C_{18}H_8O_2S_8Cl_2Br_2$: C, 29.08; H, 1.09. Found: C, 28.45; H, 1.03. Anal. Calc. for $C_{18}H_8O_2S_8ClBr_3$: C, 27.44; H, 1.02. Found: C, 27.63; H, 1.02. Quality of the crystals of $(TTF)_2$23BRQ was not good enough for the structure analysis and the composition was determined by elemental analyses alone. Anal. Calc. for $C_{18}H_8O_2S_8Cl_2Br_2$: C, 29.08; H, 1.09. Found: C, 28.81; H, 1.07. Potassium salts of the quinones were prepared by mixing cold aceton solutions of the quinones and potassium iodide. The salts were identified by IR spectra.

X-ray diffraction data were collected on a Rigaku RASA-7R 4-circle automatic X-ray diffractometer and analysed using teXan program. IR and electronic absorption spectra of the powdered samples were measured in the pressure region up to ca. 6 GPa with a diamond anvil cell. A stainless steel foil 0.03 mm thick was used as a gasket which had a hole of 0.6 mm in diameter. Nujol was used as a pressure medium and applied pressure was calibrated by the ruby fluorescence method. IR and electronic absorption spectra were recorded on a JASCO FT/IR-7000 Fourier-transform infrared spectrometer and a HITACHI U-4000 spectrophotometer, respectively. All the measurements were performed at ambient temperature.

RESULTS AND DISCUSSION

Crystal Structures

Structural data of TTF-TCLQ, $(TTF)_2$25BRQ and $(TTF)_2$TBRQ, are given in Table1 together with those of TTF-IA and $(TTF)_2$IA for comparison. In TTF-TCLQ, D and A molecules form a regular mixed column, where both TTF and TCLQ are located on the inversion center and the column axis is parallel to crystal b-axis. There exists positional disorder of chlorine and bromine atoms of the acceptor. The monoclinic structure ($P2_1/n$) is similar to that of TTF-CA[18] and not to that of TTF-IA,[13] the structure of which is triclinic ($P\bar{1}$). Interplanar distance between TTF and TCLQ is 3.43 Å: the distance is between those of TTF-CA (3.39 Å) and TTF-IA (3.57 Å) depending on the van der Waals radii of the halogen atoms. Face-to-face overlapping mode between TTF and TCLQ molecules is almost the same as that in TTF-CA.

In $(TTF)_2$25BRQ and $(TTF)_2$TBRQ, the quinone molecule is located on the inversion center and sandwiched by two TTF molecules. The crystals have no column structure but are composed of isolated TTF-quinone-TTF trimers in which the planes of the three molecules are parallel to each other. Structures of the two complexes are similar to one another and Fig. 1 shows the crystal structure of $(TTF)_2$25BRQ as an example. The structures are almost the same as that of $(TTF)_2$IA[13] except for the positional disorder of chlorine and bromine atoms in $(TTF)_2$25BRQ and $(TTF)_2$TBRQ. Interplanar distance between TTF and the quinone is 3.42 Å in $(TTF)_2$25BRQ or 3.39 Å in $(TTF)_2$TBRQ, which is smaller than that in $(TTF)_2$IA (3.53 Å). The difference is probably attributed to the smaller radii of the halogen atoms in the former complexes than that of iodine atoms

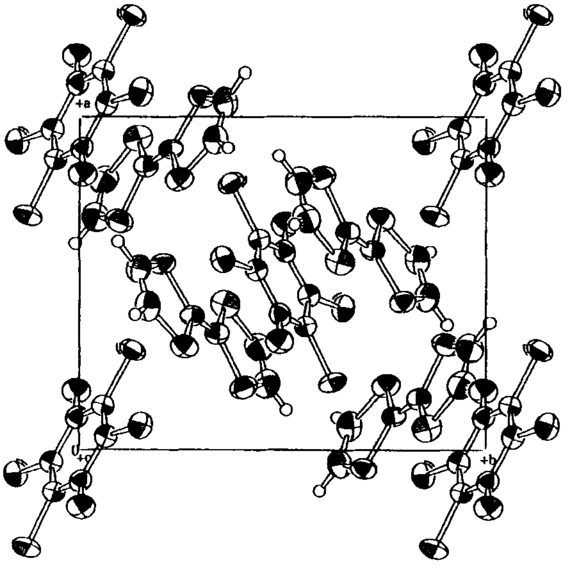

Fig. 1. Crystal structure of $(TTF)_2$25BRQ projected onto ab plane.

Table 1. Crystal data of CT complexes.

	TTF-TCLQ	(TTF)$_2$25BRQ	(TTF)$_2$TBRQ	TTF-IA[1]	(TTF)$_2$IA[1]
Chemical formula	$C_{12}H_4O_2S_4Cl_3Br$	$C_{18}H_8O_2S_8Cl_2Br_2$	$C_{18}H_8O_2S_8ClBr_3$	$C_{12}H_4O_2S_4I_4$	$C_{18}H_8O_2S_8I_4$
Formula weight	494.64	742.92	787.0	816.02	1020.36
Crystal system	monoclinic	monoclinic	monoclinic	triclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P2_1/n$
a/Å	7.445(2)	10.311(5)	10.320(1)	9.9495(2)	11.029(2)
b/Å	7.627(1)	11.729(3)	11.742(2)	7.7067(15)	12.114(2)
c/Å	14.670(2)	11.024(3)	11.035(1)	7.0898(12)	10.720(2)
α/deg	90	90	90	85.44(2)	90
β/deg	98.83(1)	110.20(3)	110.239(8)	111.27(2)	109.61(2)
γ/deg	90	90	90	114.36(1)	90
V/Å^3	823.1(2)	1251.2(9)	1254.6(3)	459.93(3)	1349.2(4)
Z	2	2	2	1	2
d_{calc}/gcm^{-3}	2.483	1.995	2.086	2.947	2.125
No. of independent reflection	1514	2208	1877	2602	2681
R/%	3.3	4.5	3.9	3.5	5.7
R_w /%	3.1	4.5	8.6	4.4	6.3

1. Ref.13 in the text.

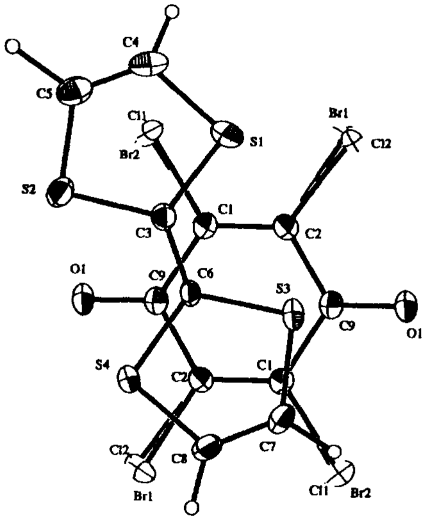

Fig. 2. Molecular overlap between TTF and 25BRQ in $(TTF)_2$25BRQ crystal.

in the latter. Figure 2 shows the face-to-face overlapping mode between TTF and 25BRQ molecules in $(TTF)_2$25BRQ crystal, which is almost the same as that between TTF and IA molecules in $(TTF)_2$IA.[13]

Bond lengths of C=C and C=O of the quinones are dependent on γ: C=C 1.343 Å and C=O 1.215 Å in TTF-TCLQ; C=C 1.345 Å and C=O 1.222 Å in $(TTF)_2$25BRQ; C=C 1.342 Å and C=O 1.207 Å in $(TTF)_2$TBRQ. In TTF-CA, C=C and C=O are 1.338 and 1.207 Å, respectively. Comparing the values with those of neutral CA (C=C 1.344 Å and C=O 1.211 Å) and ionic CA (C=C 1.35 Å and C=O 1.30 Å),[19] all the complexes studied are probably neutral at ambient pressure. The result is consistent with the ionicities estimated from IR frequencies in the following subsection.

N-I Transition

Table 2 gives IR peak frequencies of the antisymmetric C=O stretching vibration of the quinones in the four CT complexes at ambient pressure. In CT complexes of quinones, the degree of ionicity is estimated from the C=O stretching frequency on the assumption

Table 2. C=O Stretching frequency and degree of ionicity at ambient pressure together with N-I transition pressure.

	C=O Stretching frequency/cm^{-1}			Degree of ionicity	N-I transition pressure/GPa
	Complexes	Neutral quinone	Pottasium salt	(γ)	(P_c)
TTF-TCLQ	1640	1692	1522	0.21	1.1
$(TTF)_2$25BRQ	1642	1688	1520	0.28	2.0
$(TTF)_2$23BRQ	1642	1688	—	0.28	2.0
$(TTF)_2$TBRQ	1640	1688	1518	0.28	2.0

of a linear relation between the frequency and γ.[20] Also in this study, γ was estimated from the frequency of neutral quinones (γ=0) and their potassium salts (γ=1) except for 23BRQ. We attempted to prepare potassium salt of 23BRQ, but failed to obtain the salt. The failure obliged us to estimate γ of $(TTF)_2$23BRQ using the frequency of potassium salt of 25BRQ for γ=1. The C=O stretching frequency only changes in a few wavenumbers from quinone to quinone as shown in the table. Therefore, the treatment for 23BRQ may be a good approximation to estimate γ of $(TTF)_2$23BRQ. Values of γ estimated from the IR peak frequency are also given in the table. The ionicity of the donor site is a half of γ of the acceptor site since the two TTF moieties of the trimer unit are identical with one another in the crystal structures at ambient pressure as discussed in the preceding subsection.

Pressure-induced N-I transition was observed in all the complexes studied. In TTF-TCLQ, pressure dependence of the IR spectra was practically the same as that of TTF-CA.[6] A new IR peak corresponding to the antisymmetric C=O stretching vibration of the quasi-ionic acceptor molecule appeared at ca. 1.1 GPa. At this pressure, a totally symmetric C–C stretching vibration of the quinone, which is inherently IR-inactive, appeared around 950 cm^{-1} in the IR spectra. Such an appearance of totally symmetric vibrations is known to be a probe of dimerization of the regular column on the N-I transition.[21] These spectral changes clearly show the occurrence of the N-I transition of this complex at 1.1 GPa (P_c). The pressure is almost the same as that of TTF-CA (1.0 GPa).[5] The results show that the substitution of one chlorine atom of CA gives little effect to the N-I transition.

In the case of the three 2:1 complexes, N-I transition showed characteristic features different from those of $(TTF)_2$IA. Figure 3 shows the pressure-induced change of IR spectra of $(TTF)_2$25BRQ. Peak A of the antisymmetric C=O stretching vibration of 25BRQ showed a large shift to the lower frequencies with an increase in pressure. At 2.0 GPa, two new peaks (B and C) appeared as shown in Fig.3(b). On further compression, the intensities of peaks B and C increased while the intensity of peak A decreased, and then completely disappeared at 4.9 GPa as shown in Fig.3(e). Figure 4 shows the pressure dependence of the IR frequencies of $(TTF)_2$25BRQ; the right ordinate is the γ-scale for the acceptor site determined from the C=O stretching frequencies. Appearance of peak B is similar to the case of $(TTF)_2IA$[12] and γ is estimated at 0.65 from the frequency of peak B. This spectral change shows the occurrence of N-I transition at 2.0 GPa. Pressure dependence of the CT band also supports the occurrence of N-I transition. The CT transition energy decreased with increasing pressure, leveled off at 2.0 GPa, and then increased above this pressure.[22] The dependence is the same as

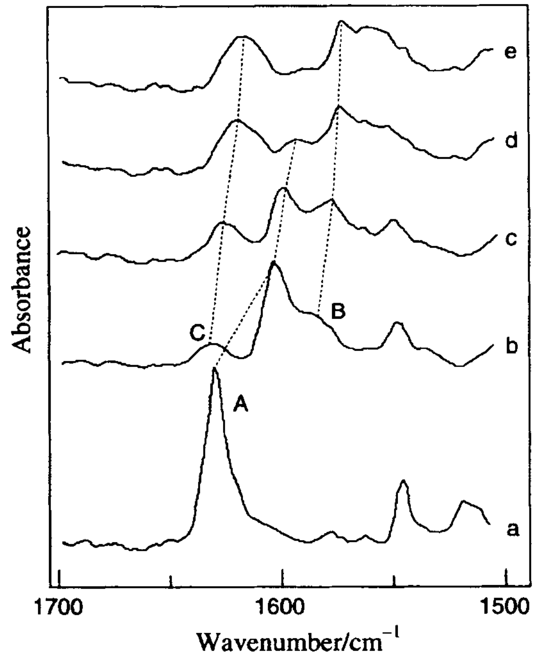

Fig. 3. Pressure-induced IR spectral change of $(TTF)_2$25BRQ in the C=O stretching region. (a) 0.5; (b) 2.4; (c) 3.2; (d) 4.4; (e) 4.9 GPa.

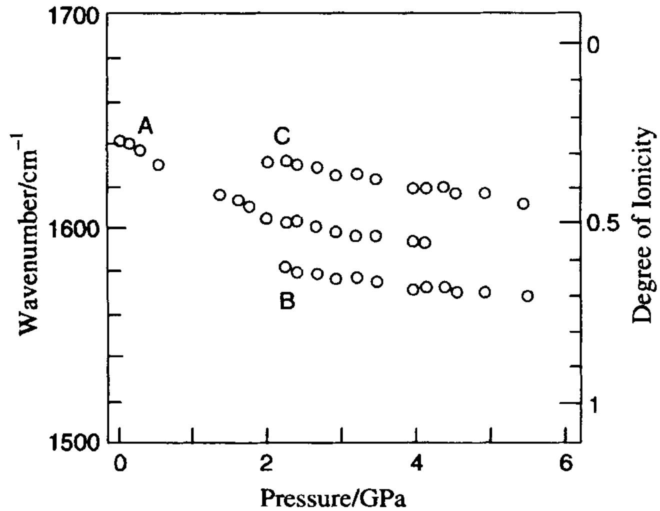

Fig. 4. Pressure dependence of C=O stretching IR frequencies of $(TTF)_2$25BRQ. Right ordinate is the γ-scale for the acceptor site determined from the C=O stretching frequency.

that observed for TTF-CA[23] and shows that this pressure is P_c of the N-I transition. The frequency of peak B further decreased with increasing pressure and γ of 25BRQ site increased up to 0.70 at 5.4 GPa which is the highest pressure for this complex in this study. IR spectra of $(TTF)_2$23BRQ and $(TTF)_2$TBRQ showed practically the same pressure dependence[22] as that of $(TTF)_2$25BRQ. The transition pressure is 2.0 GPa for all the complexes as given in Table 2. The transition pressure is fairly lower than that in $(TTF)_2$IA (3.1 GPa).[12] The lower P_c is probably due to the smaller interplanar distances between D and A in the former complexes, because smaller distances give an advantage to the ionic state through enhanced Madelung energy at lower pressure than the case of $(TTF)_2$IA.

A characteristic feature of the N-I transition in the three 2:1 complexes of this study is the appearance of peak C. This peak was observed also in

$(TTF)_2BA$[24] but not in $(TTF)_2IA$:[12] where BA is *p*-bromanil (tetrabromo-*p*-benzoquinone). The IR frequency (1632 cm^{-1}) clearly shows that the peak should be assigned to a C=O stretching vibration of the quinone. The quinone has only two C=O stretching vibrations; *i. e.*, symmetric one and antisymmetric one. Peaks A and B are assigned to antisymmetric vibrations of the low and high pressure phases, respectively. The symmetric vibration is a candidate of peak C. However, frequency of the symmetric vibration is always lower than that of antisymmetric one because of electron-molecular vibration (e-mv) coupling which only lowers the frequency of symmetric vibrations.[25] Therefore peak C is not assigned to the symmetric C=O stretching vibration of the quinone.

Another candidate is the antisymmetric vibration of the quinone of a site with lower ionicity. If this is the case, there are two quinone sites with different ionicities in the lattice. At present, character of the two sites is not clear, although the values of γ corresponding to peaks A, B and C give us a suggestion: peak A (γ=0.49), B (γ=0.65) and C (γ=0.33) at P_c. The values suggest that a couple of trimers behave cooperatively in the ionicity to give a kind of disproportionation: $2(25BRQ)^{-0.49} \rightarrow (25BRQ)^{-0.33} + (25BRQ)^{-0.65}$. With increasing pressure, the three peaks show parallel low frequency shifts with each other as shown in Fig. 4 and the above relation among the ionicities still holds at 4.1 GPa: A (γ= 0.55), B (γ=0.69) and C (γ=0.41). The result shows the same pressure dependence of the three peaks, which also supports the above assignment that peak C is the antisymmetric C=O stretching vibration of the quinone. If peak C is a symmetric stretching vibration, it is expected to show different pressure dependence with other two peaks because of the e-mv coupling affecting only symmetric stretching vibrations.[25] With decreasing pressure, the spectral changes were practically reversible except for small hysteresis near the transition point, and the spectra obtained after pressure release were the same as those before compression. The results show absence of any pressure-induced chemical reaction.

Figure 5 shows pressure-induced change of the IR spectra in the region of C–S stretching vibrations of TTF. These peaks show fairly large shifts to higher frequency (20-40 cm^{-1}) on ionization and can be used as indicators for ionicity of TTF.[26] Figure 6 shows the pressure dependence of IR frequencies of these peaks. New peak D appeared at *ca.* 3.1 GPa as shown in Fig. 5(c) and Fig. 6. This peak has been observed also in $(TTF)_2IA$[12] and is assigned to a C–S stretching vibration of ionic TTF species. The appearance of this peak is attributed to the asymmetric distribution of plus charge between the two TTF moities of a TTF-IA-TTF trimer.[14] This peak was also observed for $(TTF)_2$23BRQ and $(TTF)_2$TBRQ.[22] Therefore, the asymmetric charge distribution of TTF sites occurs in all the three 2:1 complexes in this study.

In the N-I transition of $(TTF)_2IA$,[12] the peak of the ionic TTF species appeared at P_c. In the present case, however, the pressure at which the peak appeared (3.1 GPa) is much higher than P_c (2.0 GPa); *i. e.*, the transition occurs in two steps. The result suggests that the mechanism of N-I transition in the three 2:1 complexes in this study is different from that in $(TTF)_2IA$.

Another feature of the N-I transition in 2:1 complexes is much wider region of coexistence of the low and high pressure phases compared with that of 1:1 complexes. The region is about 2 GPa for all the 2:1 complexes in this study while it is only 0.3 GPa in TTF-TCLQ[22] as well as TTF-CA.[6] Such a coexistence of the two phases is attributed to thermal excitation of the ionic state which has an energy not far from the neutral state near the transition point.[27] In 1:1 complexes with mixed column, formation of an ionic pair of D and A in the crystal lattice gives fairly large effect to the neighboring donor and

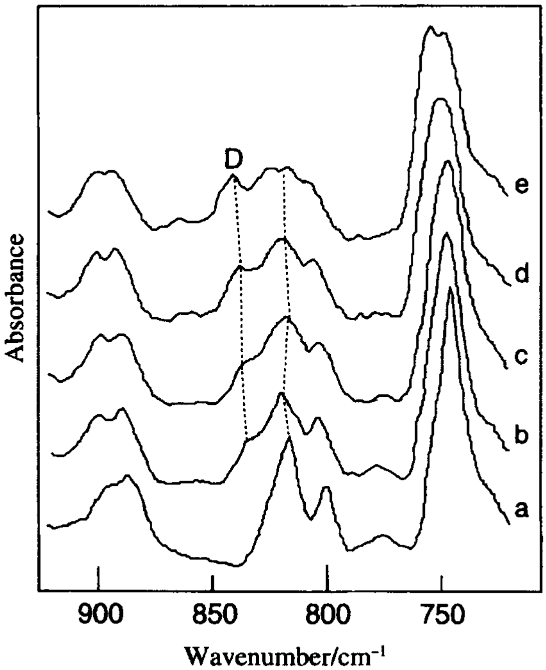

Fig. 5. Pressure-induced IR spectral change of $(TTF)_2 25BRQ$ in the C–S stretching region. (a) 0.2; (b) 2.9; (c) 3.1; (d) 3.7; (e) 4.4 GPa.

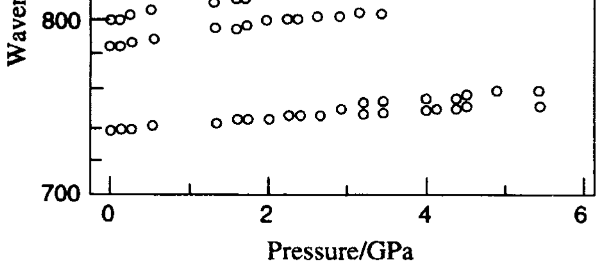

Fig. 6. Pressure dependence of C–S stretching IR frequencies of $(TTF)_2 25BRQ$.

acceptor molecules through the molecular orbital overlap between them, so that change of ionicity occurs cooperatively over a crystal domain, which promotes sudden transition and gives a narrow coexistence region. In 2:1 complexes, on the other hand, the trimer units, D–A–D, are practically independent of each other, so that formation of an ionic trimer gives minimal influence on the neighboring trimers. Therefore, the transition occurs non-cooperatively, which results in a wide coexistence region.

In general, N-I transition lowers the symmetry of the crystal lattice. In 1:1 CT complexes with mixed column, *e. g.*, TTF-TCLQ,[22] TTF-DMDCNQI[1] and TTF-CA,[8] dimerization of neighboring donor and acceptor molecules lowered the symmetry. In $(TTF)_2IA$,[12] the symmetric trimer structure in the neutral phase broke to give the asymmetric charge distribution in the ionic phase. This behavior was successfully explained by a simple trimer model.[14] In the three 2:1 complexes in this study, asymmetric charge distribution occurred not only in the donor sites but also in the acceptor sites. This means, at least, a couple of trimers behave cooperatively in the N-I transition. We may need a theoretical model treating two trimers, *i. e.*, hexamer model, to elucidate the nature of the N-I transition in this case.

DEDICATION

This paper is dedicated to Professor Yusei MARUYAMA and Professor Fumio OGURA on the occasion of their retirements from Institute for Molecular Science and Hiroshima University, respectively.

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