  Bull. Chem. Soc. Jpn., 56, 369—374 (1983)

Vibrational Spectra of Organic Conductors. Charge Transfer Salts of TTF with Substituted *p*-Benzoquinones

Susumu MATSUZAKI, Toshiharu MORIYAMA, Mitsukazu ONOMICHI,† and Koichi TOYODA*
Department of Chemistry, Faculty of Science, Kumamoto University, Kumamoto 860
†*College of Medical Technology, Kumamoto University, Kumamoto 860*
(Received May 17, 1982)

Charge transfer salts of tetrathiafulvalen (TTF) with five substituted *p*-benzoquinones (fluoranil, chloranil, bromanil, iodanil, and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone) were prepared by diffusion and cooling methods. IR, Raman, and electronic spectra of these salts measured at room temperature showed that all except fluoranil salt formed two crystal phases, *i.e.*, the diffusion and the cooling methods gave a mixed-valent and a monovalent ionic phases respectively. The degrees of charge transfer (ρ) of the mixed-valent salts were estimated from the Raman frequencies of a_g ν_3 of TTF, and nearly equal values (*ca.* 0.7) were obtained for all of them.

Since the discovery of the unusual electrical properties of TTF–TCNQ,[1] a vast amount of research has been carried out to understand the properties of the organic conductors. The research has shown that the organic charge transfer salts must satisfy two essential requirements in order to exhibit high electrical conductivity:[2] (1) The component molecules form segregated stacks of donors and acceptors; (2) charge transfer from the donor to the acceptor is incomplete, *i.e.*, $\rho<1$. At present, it is difficult to control the first requirement, whereas conditions for the satisfaction of the second requirement have been discussed considerably;[3] *i.e.*, incomplete charge transfer occurs when the difference between the ionization potential of the donor and the electron affinity of the acceptor is comparable to the crystal Madelung energy.

Determination of ρ is important to understand the conduction mechanism in organic conductors and various methods have been used to estimate the value.[4] Recently we found that the plot of Raman frequencies *vs.* ρ is linear in the case of TCNQ salts[5] and TTF salts,[6] and demonstrated that Raman spectroscopy is a useful and reliable means to estimate ρ of organic conductors.

In this work, many charge transfer salts of TTF with substituted *p*-benzoquinones are prepared by use of two different methods. The vibrational and electronic spectra of the salts are compared with each other, and the degrees of charge transfer of the mixed-valent salts are estimated from the Raman frequencies.

Experimental

TTF was synthesized by the method of Wudl *et al.*,[7] and recrystallized from hexane–cyclohexane, and sublimed twice *in vacuo*. The product was identified by spectral methods (IR and Raman) and elemental analysis. Fluoranil (tetrafluoro-*p*-benzoquinone), chloranil (tetrachloro-*p*-benzoquinone), bromanil (tetrabromo-*p*-benzoquinone), and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone were all obtained commercially, and recrystallized twice from benzene and sublimed *in vacuo*: These acceptors are abbreviated to FA, CA, BA, and DDQ respectively. Iodanil (tetraiodo-*p*-benzoquinone) was synthesized by the method of Torrey and Hunter,[8] and recrystallized several times from ethyl acetate: This acceptor is abbreviated to IA.

Charge transfer salts of TTF with the substituted *p*-benzoquinones were prepared by the following two methods: (1) Diffusion method in acetonitrile (same as reported in the literature)[9] and (2) cooling method (mixing of the stoichiometric amounts of the components in hot acetonitrile and cooling of the solution). Preparation by the diffusion method was performed at 34 ± 1 °C in evacuated H-tubes which were placed in a thermostated air bath of our own making and the periods of preparation were typically *ca.* 3 months. The composition of the salts was determined by elemental analysis.

Raman spectra of the powder samples were recorded (in the back scattering geometry) on a JASCO R-800 spectrometer equipped with NEC GLG-3200 Ar^+ and GLG-108 He–Ne lasers as exciting light sources. In order to avoid thermal decomposition of the sample, exciting laser light was focused by a cylindrical lens and sample-rotating technique was used. IR and electronic absorption spectra of the powder samples dispersed in KBr were recorded on a JASCO DS-403G IR spectrometer and a Hitachi 200-20 or a(EPS-3T) spectrophotometer, respectively. Electrical conductivity was measured bythe two probe method in an evacuated bell jar by use of a Takeda Riken TR-8561 electrometer.

Results and Discussion

TTF–FA, TTF–CA, and TTF–BA. Recently, Torrance *et al.*[10] reported that TTF formed mixed-valent crystals of good conductivity with fluoranil, whereas it formed monovalent poor conductors with chloranil and bromanil. In this work, we also have obtained a mixed-valent salt for TTF–FA by both methods, and the IR and Raman spectra are shown in Fig. 1. This salt was fairly unstable and the reproducibility of the spectra was not so good; nevertheless, the

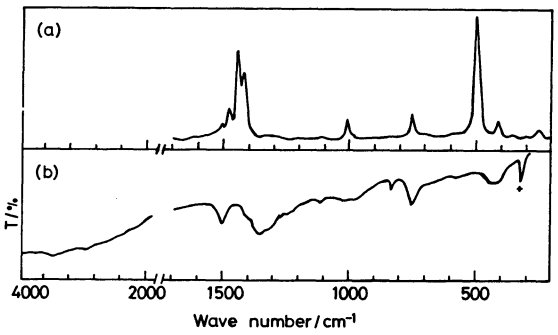

Fig. 1. Vibrational spectra of TTF–FA. (a) Raman and (b) IR; +, fault signal which is due to the exchange of gratings of the instrument.

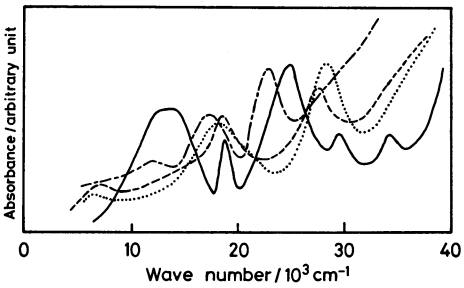

Fig. 2. Electronic spectra of TTF–CA and TTF–BA. TTF–CA(I), ------; TTF–CA(II), ——; TTF–BA(I), ·····; TTF–BA(II), —·—.

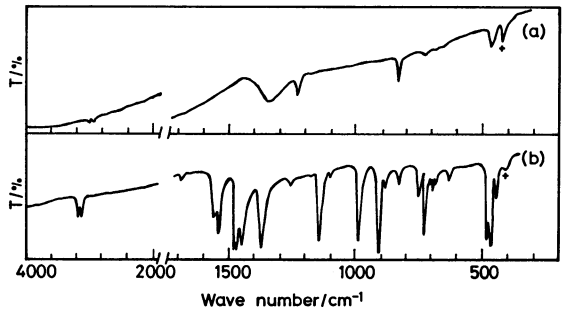

Fig. 3. IR spectra of TTF–CA. (a) TTF–CA(I) and (b) TTF–CA(II); +, fault signal which is due to the exchange of gratings of the instrument.

IR spectrum clearly shows the mixed-valency (see the discussion for TTF–CA). The Raman lines at 1443 cm^{-1} and 1418 cm^{-1} will be assigned to a_g ν_3 modes of mixed-valent and monovalent TTF cations respectively.[11] The result shows that the sample is a mixture of two salts.[12]

On the other hand, for TTF–CA and TTF–BA, we have found that the salts give a monovalent or a mixed-valent phase depending on the method of preparation.[13] The salts prepared by the diffusion method and the cooling method are represented by the symbols (I) and (II), respectively, throughout this section. Both TTF–CA(I) and TTF–CA(II) were obtained as black needles. Electronic spectra of the two salts are shown in Fig. 2. Absorption bands in the higher frequency region are assigned to LE transitions of TTF^+, which are 18500 and 27500 cm^{-1} for the salt (I), and 18700, 24700, and 29000 cm^{-1} for the salt (II).[14] Thus the result shows that both the salts contain TTF^+. In the spectrum of the salt (I), an absorption band appears at *ca.* 6700 cm^{-1} tailing to the middle infrared region (Fig. 3). It is known that mixed-valent TTF salts exhibit a low frequency band around 5000 cm^{-1} which is assigned to the mixed-valent CT transition between the neutral molecule (TTF^0) and the cation radical (TTF^+).[14,15] The band at 6700 cm^{-1} will be assigned to this CT transition, and appearance of the band strongly suggests that TTF–CA(I) is a mixed-valent salt. On the other hand, the salt (II) shows no such a low frequency band but a broad absorption band of an unusual profile at 13500 cm^{-1}. This feature will be attributed to an overlap of the two dimer-type CT bands of $(TTF^+)_2$ and $(CA^-)_2$.[15,16] The result suggests that TTF–CA(II) is a monovalent salt of dimeric structure. The salt probably corresponds to the monovalent salt reported in the literature.[10]

In the IR spectrum of TTF–CA(I), a characteristic broad band appears at 1347 cm^{-1}, whereas the corresponding band is fairly sharp in the salt (II) (Fig. 3). The component molecules have no IR-active modes in this region, and the band will be attributed to the IR-activation of a_g modes by the electron-vibration mechanism. Bozio *et al.*[11] reported that $(TTF^+)_2$ exhibits a strong IR band at 1360 cm^{-1} in DMSO solution, and assigned it to a_g ν_3 of TTF^+. Normal vibrations of the component molecules couple to each other in the dimer unit, and new normal vibrations of the dimer are produced. In the case of a_g modes, in-phase coupling modes are totally symmetric and Raman-active, whereas out-of-phase coupling modes are ungerade and IR-active. The latter promotes electron oscillation between the component radicals of the dimer, and has strong IR intensity and a lowered frequency; on the other hand the former causes no vibronic effect and the frequency is almost equal to that of the component radical.[17] Therefore, IR frequency of the out-of-phase coupling mode is usually several tens of wave numbers lower than the corresponding Raman frequency of the in-phase coupling mode. Vibronically allowed a_g modes of CA^- are also expected to be observed in the spectrum of the salt (II) because the dimerization of CA^- is suggested from the electronic spectrum as mentioned above. A strong band at 987 cm^{-1} probably arises from such an activation mechanism and will be assigned to the out-of-phase coupling mode of a_g ν_3 of CA^- because the component molecules have no IR-active fundamentals in this region and $(CA^-)_2$ was reported to show a strong IR band at 1008 cm^{-1} in potassium salt of chloranil which was assigned to this mode.[18,19]

Electronic spectra (Fig. 2) and IR spectra of TTF–BA showed characteristic features similar to those of TTF–CA. Thus it is concluded also in this case that TTF–BA(I) and TTF–BA(II) are a mixed-valent and a monovalent salts respectively. Observed IR frequencies and the tentative assignment of TTF–BA are given in Table 1 together with those of TTF–CA.

Raman spectra of TTF–CA are shown in Fig. 4. Almost all the Raman lines observed are attributable to a_g modes of TTF^+ (Table 2). This result probably arises from stronger resonance enhancement of the

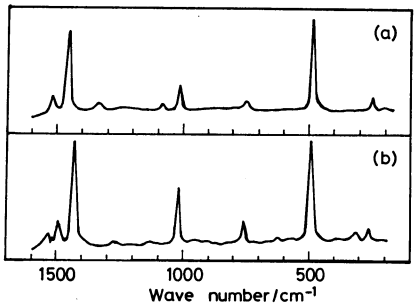

Fig. 4. Raman spectra of TTF–CA. (a) TTF–CA(I) and (b) TTF–CA(II); 514.5 nm excitation.

Table 1. Infrared frequencies of TTF-CA and TTF-BA

TTF-CA(I) $\tilde{\nu}$/cm^{-1}	TTF-CA(II) $\tilde{\nu}$/cm^{-1}	Assignment[a]	TTF-BA(I) $\tilde{\nu}$/cm^{-1}	TTF-BA(II) $\tilde{\nu}$/cm^{-1}	Assignment[a]
459 m	457 m	b_{1u} ν_{18} (TTF^+)	462 w	461 m	b_{1u} ν_{18} (TTF^+)
476 vw	476 vs	b_{1u} ν_{13} (CA^-)		616 m	b_{2u} ν_{20} (BA^-)
	484 m		639 w		
	628 w			686 s	b_{3u} ν_{28} (BA^-)
	686 w		700 w		
	696 w	b_{3u} ν_{28} (CA^-)	737 w		
731 w	725 s	b_{2u} ν_{20} (CA^-)		746 w	b_{1u} ν_{17} (TTF^+)
	750 m	b_{1u} ν_{17} (TTF^+)		821 w	
824 m	828 m	b_{1u} ν_{16} (TTF^+)	830 m	832 s	b_{1u} ν_{16} (TTF^+)
	886 w			873 vs	b_{1u} ν_{12} (BA^-)
	910 vs	b_{1u} ν_{12} (CA^-)		910 w	
	987 vs	a_g ν_3 (CA^-)	1054 m		
1072 vw		b_{1u} ν_{15} (TTF^+)	1065 m		b_{1u} ν_{15} (TTF^+)
	1171 vw			1133 w	
1236 m		b_{2u} ν_{23} (TTF^+)	1215 w	1215 vw	
	1261 w		1237 m	1246 s	b_{2u} ν_{23} (TTF^+)
1347 s, br	1370 s	a_g ν_3 (TTF^+)		1250 sh	
	1447 s		1349 s, br	1367 s	a_g ν_3 (TTF^+)
	1462 s	b_{1u} ν_{14} (TTF^+)		1482 s	b_{1u} ν_{14} (TTF^+)
	1471 sh		1500 w		
1500 w				1516 vs	b_{1u} ν_{10} (BA^-)
	1534 s	b_{1u} ν_{10} (CA^-)	1675 m		
	1545 sh	b_{2u} ν_{18} (CA^-)	3057 w	3076 w	b_{1u} ν_{13} (TTF^+)
3044 w	3044 m	b_{2u} ν_{22} (TTF^+)			
	3065 m	b_{1u} ν_{13} (TTF^+)			

a) The assginment follows Bozio *et al.* (Ref. 11) and Girlando *et al.* (Ref. 19).

Table 2. Raman frequncies[a] of TTF-CA and TTF-BA

TTF-CA(I) $\tilde{\nu}$/cm^{-1}	TTF-CA(II) $\tilde{\nu}$/cm^{-1}	Assignment[b]	TTF-BA(I) $\tilde{\nu}$/cm^{-1}	TTF-BA(II) $\tilde{\nu}$/cm^{-1}	Assignment[b]
258 w	264 m	a_g ν_7 (TTF^+)	214 m	216 m	a_g ν_5 (BA^-)
	311 m		264 m	266 m	a_g ν_7 (TTF^+)
497 vs	509 vs	a_g ν_6 (TTF^+)	391 w		
	623 m			447 w	
753 w	758 m	a_g ν_5 (TTF^+)		475 w	
	818 w		498 vs	504 s	a_g ν_6 (TTF^+)
	911 w		756 w	759 w	a_g ν_5 (TTF^+)
1013 w	1016 s	a_g ν_3 (CA^-)		905 w	
1086 w		a_g ν_4 (TTF^+)		942 w	a_g ν_3 (BA^-)
	1103 w		996 m		
	1131 w			1025 w	
	1266 w		1083 w	1090 w	a_g ν_4 (TTF^+)
1448 vs	1421 vs	a_g ν_3 (TTF^+)		1158 w	
	1481 m		1236 w	1237 w	
1524 m	1506 w	a_g ν_2 (TTF^+)	1342 w		
	1525 m	a_g ν_1 (CA^-)	1447 vs	1420 vs	a_g ν_3 (TTF^+)
			1515 m	1503 m	a_g ν_2 (TTF^+)
			1586 m	1570 m	a_g ν_2 (BA^-)
				1590 m	

a) 514.5 nm excitation. b) The assignment follows Bozio *et al.* (Ref. 11) and Girlando *et al.* (Ref. 19).

Raman lines of TTF^+ than those of CA^- with 514.5 nm excitation. We have already reported[6] that the frequency of TTF a_g ν_3 is very sensitive to the formal charge and can be a suitable measure of ρ.. This mode is observed at 1448 cm^{-1} in TTF-CA(I). The frequency is located between TTF^0 (1518 cm^{-1}) and the monovalent salt (1421 cm^{-1}), and clearly shows the mixed-valency of the salt. The salt (I) was unstable under strong laser-irradiation even by use of the cylindrical lens and the sample-rotating technique, and showed a time-dependence of the spectrum similar to that of mixed-valent TTF halides reported previously.[6] The spectrum shown in Fig. 4 was, therefore, measured under the minimized laser power (<20 mW). Kinetic study on the dependence will be reported elsewhere.[20] TTF-BA(I) and TTF-BA(II) gave the Raman spectra

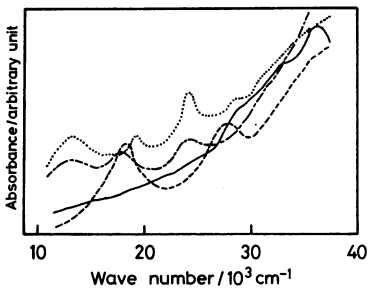

Fig. 5. Electronic spectra of TTF–IA and TTF–DDQ. TTF–IA(I), ------; TTF–IA(II), ——; TTF–DDQ(I), ·····; TTF–DDQ(II), —·—.

similar to those of TTF–CA(I) and TTF–CA(II) respectively. The frequencies and tentative assignment of the salts are given in Table 2 together with those of TTF–CA.

Electrical conductivity of TTF–CA(I) was measured to be $1\times10^{-2}\ \Omega^{-1}\ cm^{-1}$. The shape of the crystals was not so good and the maximum values were taken for the dimensions, so that the conductivity corresponds to the minimum value. This value is two to three orders of magnitude lower than those of the mixed-valent TMTTF–CA and TMTTF–BA reported by Torrance, *et al.*,[10] probably due to imperfections of the crystals in this work. Nevertheless, the value is large enough to demonstrate the mixed-valency of TTF–CA(I).

Stoichiometries of TTF–CA(II) and TTF–BA(II) were found to be 1 : 1 by the elemental analyses, but the values of the salts (I) varied from 2 : 1 to 1 : 2. This variation probably arises from mixing of the component molecules with the crystals of the salts, because it was observed by an optical microscope that yellow areas scattered on the black surface of the crystals. Thus the compositions of the salt (I) are unknown at present. It has been reported that TMTTF forms the mixed-valent salts of 1 : 1 stoichiometry with chloranil and bromanil,[10] and it seems natural to consider the 1 : 1 stoichiometry also in the present case.

TTF–IA. TTF–IA(I) and TTF–IA(II) were obtained as black powder and black needles respectively. Electronic spectra of the two salts are much different from one another (Fig. 5). TTF–IA(II) shows no absorption bands around 18000 cm^{-1}, so that it contains no TTF^+ species; furthermore, IR and Raman spectra (Figs. 6 and 7) of the salt are reasonably explained as an overlapp of those of TTF^0 and IA^0 (Tables 3 and 4). The result shows that the salt (II) is a non-ionic CT complex and will be an analog of the neutral mixed-stack crystals of TTF–CA and TTF–BA reported by Mayerle *et al.*[21] On the other hand, the absorption bands of TTF^+ appear in the electronic spectrum of TTF–IA(I) (Fig. 5); furthermore, the IR spectrum shows apparent similarity to that of the mixed-valent TTF–CA(I) (Figs. 6 and 3). The Raman spectrum also shows the mixed-valent TTF $a_g\ \nu_3$ line at 1448 cm^{-1} (Fig. 7). It is, therefore, evident that TTF–IA(I) is a mixed-valent salt.[22]

No vibrational assignment has been reported for the Raman-active fundamentals, and we have assigned them by referring to the assignment for chloranil and bromanil by Girlando *et al.*[19] As given in Table 4, main Raman lines are reasonably assigned on the basis of the rule that the frequency must be lowered because of the larger atomic weight of iodine than chlorine and bromine. Assignment of the IR-active vibrations has been reported by Iida,[23] and we use the result in this study.

Several vibrational features show fairly large frequency shifts (20—40 cm^{-1}) by the complex formation, *e.g.*, ν_1 and ν_{10} of iodanil, and ν_3 of TTF (the frequency of TTF^0 is 1518 cm^{-1}). The result shows the fairly strong CT interaction operating between TTF and iodanil in this non-ionic CT complex. The degree of charge transfer is estimated to be 0.3 from the ν_3 frequency of TTF assuming that the linear relation between the frequency and ρ is valid for mixed-stack complexes.

IR spectrum of this non-ionic CT complex is influenced by the vibronic effect as in the radical salts. A

Table 3. Infrared frequencies of TTF–IA

TTF–IA(I) $\tilde{\nu}/cm^{-1}$	TTF–IA(II) $\tilde{\nu}/cm^{-1}$	Iodanil $\tilde{\nu}/cm^{-1}$	Assignment[a]
460w	439 s		$b_{1u}\ \nu_{18}$ (TTF)
	491w		
		535 vw	
568 vw	565m	570 s	$b_{2u}\ \nu_{20}$ (IA)
	576 vw	580w	
	615w		
		628 vw	
	646 s		$b_{3u}\ \nu_{34}$ (TTF)
	664 s		
	686 s	694 s	$b_{3u}\ \nu_{28}$ (IA)
	733m		$b_{1u}\ \nu_{17}$ (TTF)
	780m		$b_{1u}\ \nu_{16}$ (TTF)
	793 s		$b_{1u}\ \nu_{25}$ (TTF)
818 sh	806 vw		
824w		825 vw	
	843m	842w	$b_{1u}\ \nu_{12}$ (IA)
	866 vw		
1015m	1017 vs	1019 vs	$b_{1u}\ \nu_{11}$ (IA)
	1031w	1029w	
	1087 vw		
	1095m		$b_{1u}\ \nu_{15}$ (TTF)
	1158w	1150 sh	
1171w	1172 s	1177 vs	$b_{2u}\ \nu_{19}$ (IA)
	1187 sh	1194w	
1240m	1255 s		$b_{2u}\ \nu_{23}$ (TTF)
		1269w	
1344 s, br			$a_g\ \nu_3$ (TTF^+)
		1362m	
		1500 sh	
	1487 vs		$a_g\ \nu_3$ (TTF)
1518w		1520 vs	$b_{2u}\ \nu_{18}$ (IA)
	1540m		
		1554w	
	1562w		
1663m	1633 vs	1659 vs	$b_{1u}\ \nu_{10}$ (IA)
3044w	3061m		$b_{2u}\ \nu_{22}$ (TTF)
	3082w		

a) The assignment of IR-active fundamentals follows Iida (Ref. 23).

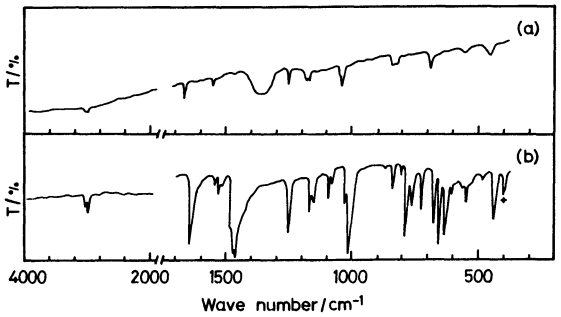

Fig. 6. IR spectra of TTF–IA. (a) TTF–IA(I) and (b) TTF–IA(II); +, fault signal which is due to the exchange of gratings of the instrument.

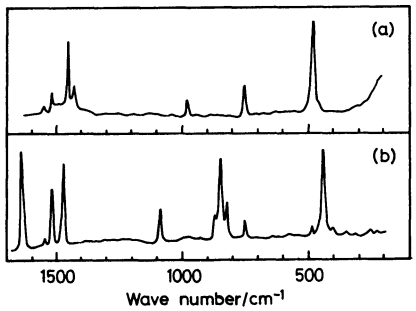

Fig. 7. Raman spectra of TTF–IA. (a) TTF–IA(I) and (b) TTF–IA(II); 514.5 nm excitation.

strong IR band at 1487 cm^{-1} has the same frequency as the Raman line of TTF a_g ν_3 (Tables 3 and 4) and will be assigned to this mode. In the case of mixed-stack CT complexes, the normal vibration of totally symmetric modes itself promotes the electron oscillation between the donor and the acceptor. Therefore, the IR frequency is equal to the Raman frequency, in contrast to the case of the segregated-stack radical salts of dimeric structure where the Raman and IR intensities are induced by the in-phase and out-of-phase coupling modes respectively. It may also be possible to assign the band at 1487 cm^{-1} to b_{2u} ν_{18} of iodanil. However, it is hard to accept from the standpoint of the frequency shift. Ion radical of iodanil has not yet been prepared and the frequency shift by full charge transfer ($\rho=1$) is unknown, but the shifts in chloranil and bromanil were reported to be 27 and 20 cm^{-1} respectively.[19] Therefore, it is not reasonable to expect that the shift of 33 cm^{-1} occurs in the present case of the partial charge transfer ($\rho=0.3$).

TTF–DDQ. Electron affinities of all the tetrahalo-*p*-benzoquinones are practically equal to each other; on the other hand, DDQ has the fairly larger value than the others.[24] Therefore, formation of the mixed-valent phase was considered to be difficult. The cooling method gave the monovalent salt, TTF–DDQ(II), as evident from the spectra (Figs. 5, 8, and 9). Mayerle and Torrance[25] reported the formation of single crystals of the monovalent salt by the diffusion method. The samples obtained by this method were mostly the monovalent salt also in this work; nevertheless, a few samples, TTF–DDQ(I),[26] showed the characteristic IR

Table 4. Raman frequencies[a] of TTF–IA

TTF–IA(I) $\tilde{\nu}$/cm^{-1}	TTF–IA(II) $\tilde{\nu}$/cm^{-1}	Iodanil $\tilde{\nu}$/cm^{-1}	Assignment
	452 vs	472 vs	a_g ν_4 (IA)
493 vs	490 w		a_g ν_6 (TTF)
753 m	732 w		a_g ν_5 (TTF)
	844 s	846 m	
	869 vs	872 s	a_g ν_3 (IA)
989 w			
	1095 m		a_g ν_4 (TTF)
		1200 w	
1417 m			a_g ν_3 (TTF^+)[b]
1448 s	1486 vs		a_g ν_3 (TTF)
	1529 vs	1543 vs	a_g ν_2 (IA)
1512 m	1543 m		a_g ν_2 (TTF)
	1615 vs	1654 vs	a_g ν_1 (IA)

a) 514.5 nm excitation. b) This line is probably attributable to a monovalent TTF^+ contained as an impurity.

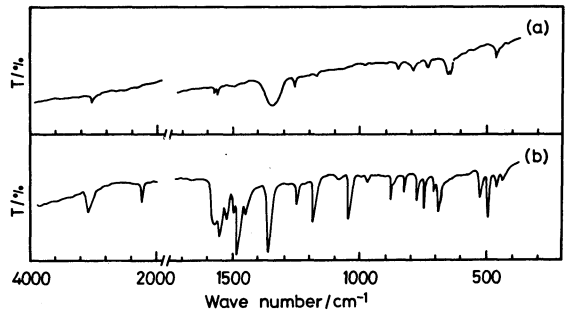

Fig. 8. IR spectra of TTF–DDQ. (a) TTF–DDQ(I) and (b) TTF–DDQ(II).

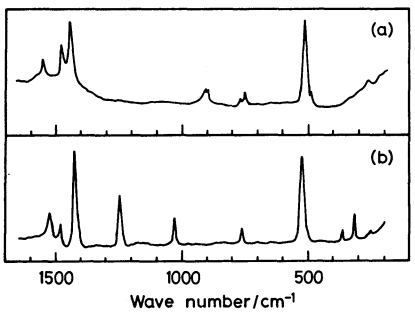

Fig. 9. Raman spectra of TTF–DDQ. (a) TTF–DDQ(I) and (b) TTF–DDQ(II); 514.5 nm excitation.

and Raman spectra of the mixed-valent salt (Figs. 8 and 9). Raman lines at 1423 and 1453 cm^{-1} are assigned to a_g ν_3 modes of the monovalent and the mixed-valent TTF cations respectively. Relative intensity of the two lines shows that the fraction of the mixed-valent salt is small, *i.e.*, the salt is not so easy to be formed. The result is consistent with the large electron affinity of DDQ.

Estimation of ρ. In the case of TTF salts, it has been shown that the ν_3 mode gives the best result for the estimation of the degree of charge transfer (ρ).[6] In this investigation, therefore, the values of ρ of the mixed-valent salts were estimated from the ν_3 frequencies by use of the calibration curve obtained previously. The

values of ρ thus obtained are: 0.75 (TTF–FA); 0.71 (TTF–CA); 0.72 (TTF–BA); 0.71 (TTF–IA); and 0.66 (TTF–DDQ). These values inherently contain uncertainty because of the crystal field effect on the frequency.[5] The uncertainty is estimated to be 0.1 for TTF ν_3 from the frequency variation of many monovalent salts of TTF. Therefore, it should be considered that the mixed-valent salts in this work have the values of ρ which are practically equal to each other.[27] The degree of charge transfer is determined by the two quantities, $(I-A)$ and E_M, in the mixed-valent salt of the segregated structure,[2,3] where $(I-A)$ is the difference between the ionization potential (I) of the donor and the electron affinity (A) of the acceptor, and E_M is the crystal Madelung energy. If $(I-A)>E_M$, neutral ground state is more stable in energy and, on the contrary, ionic ground state is favorable if $(I-A)<E_M$. The mixed-valent state will be realized when $(I-A)\simeq E_M$. The tetrahalo-*p*-benzoquinones have the electron affinities which are almost equal to each other, and $(I-A)$ is practically constant in all the mixed-valent salts except the DDQ salt. The result of the practically equal values of ρ, therefore, suggests that E_M is almost constant in all the salts, *i.e.*, the crystal structures are similar to each other. On the other hand, the electron affinity of DDQ is fairly large;[24] therefore, it may be difficult to explain the value of ρ from this standpoint. X-ray structural analyses of these salts are necessary for further discussion.

The present work was partially supported by a Grant-in-Aid for Scientific Research No. 56470009 from the Ministry of Education, Science and Culture.

References

1) M. J. Cohen, L. B. Coleman, A. F. Garito, and A. J. Heeger, *Phys. Rev. B*, **10**, 1298 (1974).
2) J. B. Torrance, "Synthesis and Properties of Low-Dimensional Materials," Ann. N. Y. Acad. Sci. (1978), p. 210.
3) J. B. Torrance and B. D. Silverman, *Phys. Rev. B*, **15**, 788 (1977); J. B. Torrance, *Acc. Chem. Res.*, **12**, 79 (1979).
4) S. Megtert, J. P. Pouget, and R. Comes, in Ref. 2, p. 234; P. Coppens and T. N. Guru Row, in Ref. 2, p. 244; F. Devreux and M. Nechtshein, "Quasi One-Dimensional Conductors. I," ed by S. Barisic, A. Bjelis, J. R. Cooper, and B. Leontic, Springer-Verlag, Berlin (1979), p. 153.
5) S. Matsuzaki, R. Kuwata, and K. Toyoda, *Solid State Commun.*, **33**, 403 (1980).
6) S. Matsuzaki, T. Moriyama, and K. Toyoda, *Solid State Commun.*, **34**, 857 (1980).
7) F. Wudl, M. L. Kaplan, E. J. Hufnagel, and E. W. Southwick, Jr., *J. Org. Chem.*, **39**, 3608 (1974).
8) H. A. Torrey and W. H. Hunter, *J. Am. Chem. Soc.*, **34**, 702 (1912).
9) J. R. Andersen, E. M. Engler, and K. Bechgaard, in Ref. 2, p. 293.
10) J. B. Torrance, J. J. Mayerle, V. Y. Lee, and K. Bechgaad, *J. Am. Chem. Soc.*, **101**, 4747 (1979).
11) R. Bozio, I. Zanon, A. Girlando, and C. Pecile, *J. Chem. Phys.*, **71**, 2282 (1979).
12) Spectra of the pure sample of mixed-valent TTF–FA have not yet been obtained because the salt was fairly unstable and decomposed rapidly to a monovalent salt by laser-irradiation.
13) Neutral mixed-stack crystals of TTF–CA and TTF–BA reported in Ref. 21 have not been obtained in this work.
14) T. Sugano, K. Yakushi, and H. Kuroda, *Bull. Chem. Soc. Jpn.*, **51**, 1041 (1978).
15) J. B. Torrance, B. A. Scott, B. Welber, F. B. Kaufman, and P. E. Seiden, *Phys. Rev. B*, **19**, 730 (1979).
16) S. Hiroma and H. Kuroda, *Bull. Chem. Soc. Jpn.*, **46**, 3645 (1973).
17) M. J. Rice, *Solid State Commun.*, **31**, 93 (1979).
18) R. Bozio, A. Girlando, and C. Pecile, *Chem. Phys.*, **21**, 257 (1977).
19) A. Girlando, I. Zanon, R. Bozio, and C. Pecile, *J. Chem. Phys.*, **68**, 22 (1978).
20) T. Moriyama, S. Matsuzaki, and K. Toyoda, to be published.
21) J. J. Mayerle, J. B. Torrance, and J. I. Crowley, *Acta Crystallogr., Sect. B*, **35**, 2988 (1979).
22) A Raman line at 1417 cm^{-1} is assigned to a_g ν_3 of TTF^+. Appearance of this line shows that TTF–IA(I) was contaminated by a monovalent salt. The amount is probably very small because the intensity of the Raman line is weak: The line has very large intensity in monovalent salts (Fig. 4).
23) Y. Iida, *Bull. Chem. Soc. Jpn.*, **50**, 1337 (1977).
24) E. C. M. Chen and W. E. Wentworth, *J. Chem. Phys.*, **63**, 3183 (1975).
25) J. J. Mayerle and J. B. Torrance, *Bull. Chem. Soc. Jpn.*, **54**, 3170 (1981).
26) Amount of the salt (I) obtained was so small that the elemental analysis was not feasible.
27) TTF–FA and TTF–DDQ seem to have a larger and a smaller values than the others respectively; however, taking into account the uncertainty, the differences should not be regarded as significant at present.