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X-Ray Photoelectron Spectroscopic Study of Tetrathiafulvalene–Tetracyanoquinodimethane (TTF·TCNQ) and Related High Conductive Organic Complexes

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Tetrathiafulvalene–tetracyanoquinodimethane (TTF·TCNQ) and related high conductive organic complexes were studied by X-ray photoelectron spectroscopy (XPS). The N 1s peak shape of TTF·TCNQ evaporated film was found to change by X-ray irradiation; the high-binding energy shoulder of the N 1s peak increased its intensity with X-ray irradiation time and finally showed a new peak separated by about 1.5 eV from the main peak. TTF·TCNQ was found to be 1:1 both in the surface and in the bulk. The amounts of charge transfer in TTF·TCNQ and other TTF complexes as well as those in 5,6:11,12-bis(dithio)naphthacene(tetrathiotetracene, TTT) complexes were determined from the analysis of the S 2p peak shape. The amount of charge transfer is 0.56 ± 0.05 in TTF·TCNQ and 0.55 ± 0.05 in TTF·TNAP (tetracyanonaphthoquinodimethane). The molecular ratio of $(donor)^+$ in donor molecules is 0.71 ± 0.05 in $TTF\cdot Br_{0.7}$, 0.52 ± 0.05 in $TTF\cdot I_{0.7}$, 0.65 ± 0.05 in $(TTF)_3(BF_4)_2$, 0.49 ± 0.05 in $(TTT)_2I_3$, and 0.93 ± 0.05 in $(TTT)(TCNQ)_2$, which correspond respectively to 100, 73, 100, 100, and 100% charge transfer between donors and acceptors. The N 1s peak shape of TTF·TCNQ is also discussed.

The charge-transfer salt, tetrathiafulvalene–tetracyanoquinodimethane (TTF·TCNQ), is a typical example of the organic solid that exhibits the behaviors as a quasi-one-dimensional conductor. The crystal of TTF·TCNQ was initially considered to be composed of TTF^+ and $TCNQ^-$ as a result of a complete charge transfer from TTF to TCNQ. However, several experimental evidences were accumulated later to indicate that the charge transfer between TTF and TCNQ is not complete.[1–10]

There are a variety of highly-conductive charge-tranfer salts which involve TTF or its analogs as the electron donor and/or TCNQ or its analogs as the electron acceptor. In almost all cases of these metal-like conductors, donor stacks and/or acceptor stacks are in a mixed-valence state as in TTF·TCNQ. It is now believed that this mixed-valence character has an important bearing on the metallic behaviors of these organic solids.

X-Ray photoelectron spectroscopy (XPS) could provide informations concerning the electronic state of a mixed-valence molecular stack. If holes in a donor stack (or electrons in an acceptor stack) are highly localized, each core electron peak in the XPS spectrum will be composed of the components corresponding to the neutral molecule and the ion, respectively. On the other hand, if holes in a donor stack (or electrons in an acceptor stack) are completely delocalized, the core electron peaks will be of single component corresponding to the partially ionized state of the molecule.[11]

Some years ago, we first reported the results of the XPS studies on a series of TCNQ salts.[12,13] As compared with the N ls peaks of TCNQ simple salts, the N ls peaks were found to be significantly broader in the XPS spectra of TCNQ complex salts, as if it is composed of the peaks due to the neutral molecule and ion of TCNQ. However, the observed peak shapes could not be satisfactorily reproduced by the simple superposition of the N ls peak of $TCNQ^0$ and that of $TCNQ^-$.[13] In the XPS spectra of TCNQ salts, the N ls peaks are always accompanied by a strong shake-up satellite, which seems to vary depending on the intermolecular charge-transfer interaction within a TCNQ stack. This introduces a considerable complexity into the analysis of the observed peak profile. In contrast, the S 2p peak of TTF is not accompanied by a strong satellite. Thus it seems worthwhile to see if the S 2p peak profiles in the XPS spectra of TTF salts can be well interpreted by the superposition of the components associated with TTF^0 and TTF^+.

There is another aspect which should be examined in order to establish the interpretation of the XPS spectra of TTF·TCNQ and related materials. The chemical composition in the surface region could be different from the bulk. In effect, it was pointed out by Ritsko *et al.*,[14] from the XPS studies of an evaporated film of TTF·TCNQ, that the surface of a TTF·TCNQ film prepared at room temperature was more nitrogen rich than the bulk. Thus we tried to know if there is actually any significant difference between the bulk and surface by means of the observation of the angular dependence of the XPS spectrum.

In the present paper, we will report the results of these XPS studies made on a series of TTF salts and related materials.

Experimental

Materials. The chemical formulae of the organic donors and acceptors used in the present study are given in Fig. 1.

TTF, TTT, and TNAP were synthesized according to the literatures.[15–19] Other compounds were commercially obtained.

The crystalline powders of the charge-transfer salts were prepared by the procedures described in the literatures.[18,20–22] In the cases of the bromide and iodide of TTF, the mole ratio of donor and acceptor is known to vary depending on the condition of preparation.[20,21] We obtained $TTF\cdot Br_{0.7}$ and $TTF\cdot I_{0.7}$ by the methods given in our previous paper.[15]

XPS Measurements. X-Ray photoelectron spectra were

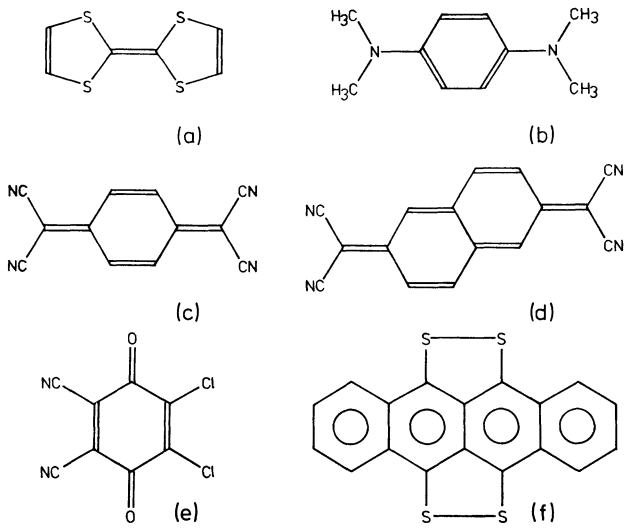

Fig. 1. (a) Tetrathiafulvalene (TTF), (b) *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD), (c) tetracyanoquinodimethane (TCNQ), (d) tetracyanonaphthoquinodimethane (TNAP), (e) 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ), (f) 5,6:11,12-bis(dithio)naphthacene (tetrathiotetracene, TTT).

measured with a McPherson ESCA 36 electron spectrometer using Mg $K\alpha$ (1253.6 eV) as the stimulating radiation. In all cases except K·TCNQ, TTF·TNAP and TTT salts, samples were deposited onto aluminum plates by the sublimation within the sample chamber of the spectrometer. XPS measurements were also done on powder samples pressed onto aluminum plates. The spectra thus obtained were almost the same as those obtained with evaporated films. To measure the spectrum of TTF solid, the sample was deposited onto an aluminum substrate cooled with a dry ice–ethanol mixture in order to reduce the evaporation of TTF.

The binding energies of photoelectron peaks were calibrated by using the Au $4f_{7/2}$ peak (83.8 eV) of a thin gold film deposited on the sample surface.

To vary the photoelectron take-off angle, an angle-variable sample holder was specially designed so as to be incorporated into our XPS spectrometer. The details of this sample holder will be reported elsewhere.[23]

Results and Discussion

Angular Dependence of XPS Spectrum of TTF·TCNQ and the Effects of X-Ray Irradiation. We measured the XPS spectrum of an evaporated film of TTF·TCNQ setting the photoelectron take-off angle θ, measured from the sample plane, at 10° and at 80°. We noted that the shape of N ls peak changed with time as we repeated XPS measurements on the same sample. Figure 2 shows the variation of the N ls peak shape with X-ray irradiation time, observed under the conditions that $\theta=80°$. The intensity at the high-binding energy shoulder of the N ls peak increased with irradiation time, and finally showed a new peak separated by about 1.5 eV from the main peak. The irradiation effect did not appear so clearly in the spectra measured at $\theta=10°$. In this case, the

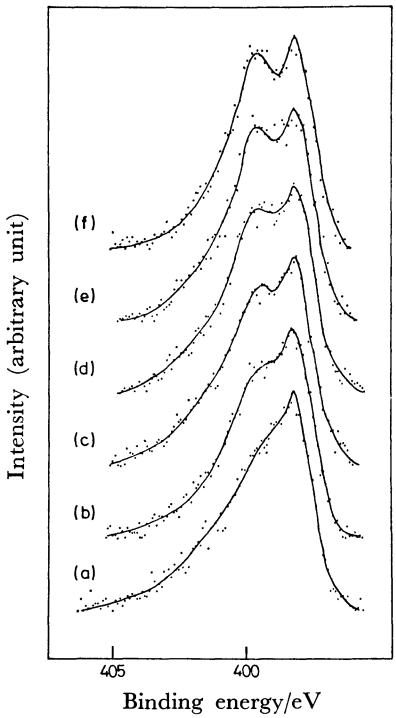

Fig. 2. The variation of the N 1s peak shape of TTF·TCNQ evaporated film with X-ray irradiation time. (The photoelectron take-off angle is 80°.)
X-Ray irradiation time: (a) 0 min, (b) 200 min, (c) 465 min, (d) 630 min, (e) 795 min, and (f) 960 min.

change of the N ls peak shape was almost negligible after 400 min irradiation while a significant change was observable with the same film when $\theta=80°$.

It is well established that, when the angular distribution of XPS spectrum is measured on a very flat surface of a solid sample, the contribution of the surface relative to that of the bulk increases with the decrease of the photoelectron take-off angle. It was discussed by Fadley *et al.* that the same tendency can be also expected when the sample is an evaporated film with considerable surface roughness.[24] However, an opposite interpretation was taken by Ritsko *et al.*, in the case of the TTF·TCNQ evaporated film.[14] They observed by a scanning electron microscope that needle crystals of TTF·TCNQ are standing up on the substrate. From this structure of the film, they considered that the XPS spectrum obtained at a high take-off angle must reflect the surface state more strongly than the spectrum obtained at a low take-off angle. This interpretation seems to be consistent with our results concerned with the X-ray irradiation effect, since, in our experiments, the change of the N ls peak shape was markedly observed in the spectra measured at $\theta=80°$, not at $\theta=10°$, while the change by X-ray irradiation is naturally expected to take place rather in the surface region than in the bulk.

We found no appreciable change by X-ray irradiation in the S 2p peak shape, even if a marked change had already taken place in the N ls peak of the same sample.

We estimated the N/S atomic ratio from the in-

Table 1. Angular dependent XPS results of TTF·TCNQ evaporated films

	Run	Measured peaks	X-Ray irradiation time / min	Take-off angle/°	N/S atomic ratio
Exp. I	1	S 2p, N 1s	0	80	1.00 : 1
	2	S 2p, N 1s	100	10	0.96 : 1
	3	S 2p, N 1s	200	80	1.00 : 1
	4	S 2p, N 1s	300	10	0.90 : 1
	5	S 2p, N 1s	465	80	0.96 : 1
	6	S 2p, N 1s	630	80	0.96 : 1
Exp. II	1	S 2p, N 1s	0	10	0.94 : 1
	2	S 2p, N 1s	100	80	0.93 : 1
	3	S 2p, N 1s	200	10	0.89 : 1
Exp. III	1	S 2p, N 1s	0	10	0.94 : 1
	2	S 2p, N 1s	100	80	0.99 : 1
	3	S 2p, N 1s	200	10	0.98 : 1
	4	S 2p, N 1s	300	80	0.98 : 1
Exp. IV	1	S 2p, N 1s	0	80	0.96 : 1
	2	S 2p, N 1s	100	10	0.94 : 1
Exp. V	1	S 2p, N 1s	0	10	0.95 : 1
	2	S 2p, N 1s	100	80	0.99 : 1

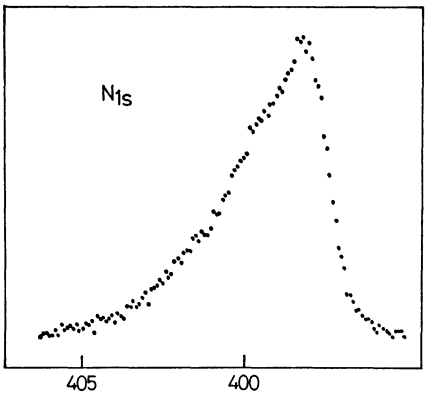

Fig. 3. The intrinsic N 1s peak of TTF·TCNQ. (Refer the text.)

tegrated intensities of the N ls and S 2p peaks.[25] The results are given in Table 1. In each experiment, an evaporated film of TTF·TCNQ was freshly prepared, and the N ls and S 2p peaks were repeatedly recorded by setting the take-off angle at either 10° or 80°. The results show that the N/S atomic ratio does not vary on X-ray irradiation in spite of the change of the N ls peak shape. It should be noted also that the atomic ratio is the same within the experimental error between the cases $\theta=10°$ and 80°, the average value being 0.94 ± 0.03 for $\theta=10°$ and 0.96 ± 0.04 for $\theta=80°$. This fact may indicate that the mole ratio of TTF and TCNQ is not significantly different between the surface and the bulk, and does not vary with X-ray irradiation.

The mechanism that causes the change of the N ls peak shape of TTF·TCNQ is not clear at present. The new peak which appeared at the high-binding energy side of the main peak after a long X-ray irradiation could correspond to the N ls peak due to $TCNQ^0$.[9] If this is the case, we should consider that the ratio of TCNQ neutral molecule to $TCNQ^-$ ion increased in the surface region by X-ray irradiation. One could suspect that this change of the $TCNQ^0/TCNQ^-$ ratio is associated with a partial loss of TTF molecules from the surface region. But this is not likely to be the case since the N/S atomic ratio did not change with X-ray irradiation. If the new peak is attributable to $TCNQ^0$, a possible interpretation for the appearance of this peak could be that the electron transfer from $TCNQ^-$ to some adsorbed chemical species is enhanced by some way with X-ray irradiation. But we cannot exclude the possibility that the new peak is associated not with $TCNQ^0$, but with some product of an X-ray induced chemical reaction.

In any case, it is of vital importance to record the N ls peak with a fresh film minimizing X-ray irradiation time in order to get the true peak shape. We summed up the data obtained within a short measuring time on several freshly-deposited TTF·TCNQ films, and obtained the N ls peak shape which is shown in Fig. 3. This can be taken as the true N ls peak shape without the deformation due to X-ray irradiation. It is very asymmetric with a long tail in the higher binding energy side. This is considerably different from the N ls peak shapes which were reported by other authors.[6,14] The peak shapes hitherto reported seem to correspond to the state which has been already affected by X-ray irradiation.

Peak Shape and Degree of Charge Transfer. The S 2p spectra of TTF, $(TTF)^+\cdot(DDQ)^-$, TTT, and $(TTT)^+\cdot(ClO_4)^-$ are shown in Fig. 4. In each case, the observed spectrum shows a peak corresponding to S $2p_{3/2}$ and a shoulder corresponding to S $2p_{1/2}$. The overall fwhm (full width at half-maximum height) is 2.1 eV in the cases of TTF and TTT, and 2.5 eV in the cases of $(TTF)^+\cdot(DDQ)^-$ and $(TTT)^+\cdot$

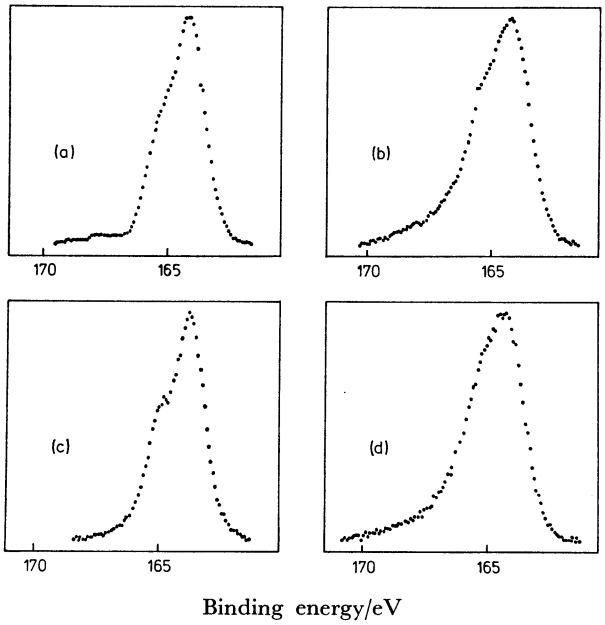

Fig. 4. S 2p peaks in the XPS spectra of (a) TTF, (b) TTF·DDQ, (c) TTT, and (d) TTT·(ClO_4).

$(ClO_4)^-$.[26] Any strong shake-up satellite does not appear in these S 2p spectra.

The S 2p spectra of TTF·$Br_{0.7}$, TTF·$I_{0.7}$, $(TTF)_3(BF_4)_2$, TTF·TCNQ, and TTF·TNAP are shown in Fig. 5. The peak profiles observed in these cases are significantly different from those shown in Fig. 4, showing a larger peak width; the fwhm is 2.7—3.1 eV in these cases. Obviously, TTF stacks in TTF·$Br_{0.7}$ and TTF·$I_{0.7}$ are in a mixed-valence state. From the chemical composition of TTF·$Br_{0.7}$, one can expect that about 70 percent of TTF molecules are in the state of TTF^+ and the remaining 30 percent are in the state of TTF^0, provided that all bromine atoms are in the state of Br^-. As shown in Fig. 5, the S 2p spectrum of TTF·TCNQ is similar to those of TTF·$Br_{0.7}$ and TTF·$I_{0.7}$, and distinctly different from those of $(TTF)^+\cdot(DDQ)^-$ and $(TTF)^+\cdot(ClO_4)^-$. This fact suggests that an incomplete charge transfer is taking place in TTF·TCNQ.

Assuming that the observed S 2p peak profile of $(TTF)^+\cdot(DDQ)^-$ is the one characteristic of TTF^+ and that of TTF is the one characteristic of TTF^0, we tried to reproduce the observed peak profiles of mixed-valence TTF salts by superimposing these two standard peak profiles, treating their separation and relative intensities as adjustable parameters. We defined the following error function:

$$R = \sum_i |I_{obsd}(E_i) - I_{calcd}(E_i)|/I_{obsd}(E_i)$$

where $I_{obsd}(E_i)$ is the observed intensity at the binding energy E_i and $I_{calcd}(E_i)$ is the calculated intensity of the superimposed peak profile at the same binding energy. We calculated the R value for each assumed parameter set and looked for the minimum point of the R map, which was taken to give the parameter set for the best fit between the observed and calculated peak profiles. All of these calculations were performed by use of a computer HITAC 8700/8800 at the Computer Center, University of Tokyo. The final results of the simulations for the mixed-valence TTF salts are shown in Fig. 5 with solid lines. The TTF^0 and TTF^+ components are shown in the same figure with broken lines. The results shown in Fig. 5 indicate that the S 2p peak profiles observed of the mixed-

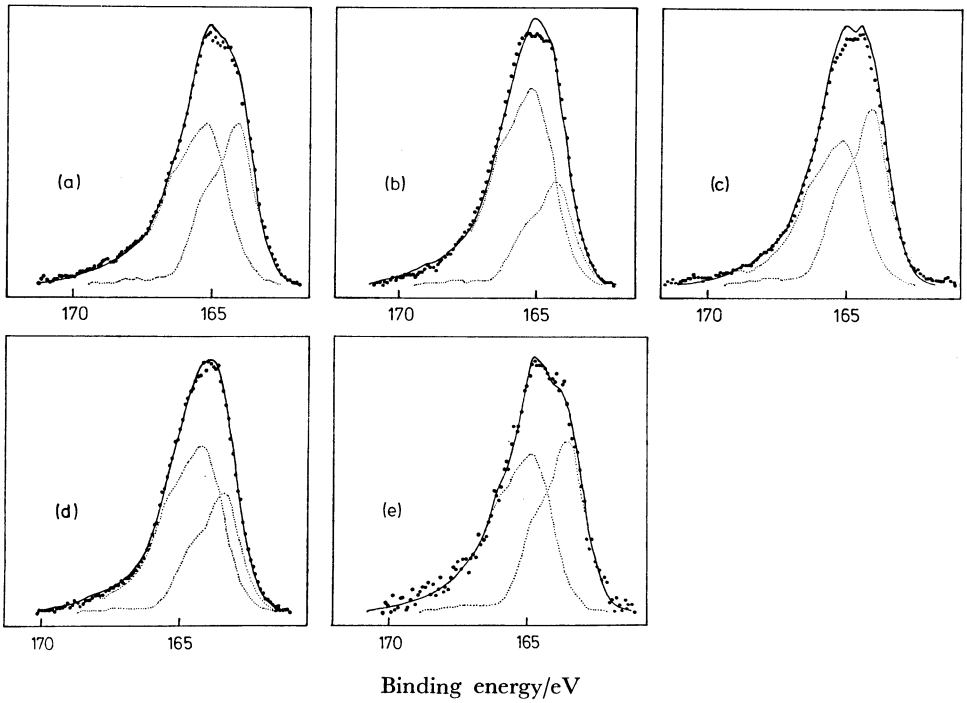

Fig. 5. S 2p peaks in the XPS spectra of (a) TTF·TCNQ, (b) TTF·$Br_{0.7}$, (c) TTF·$I_{0.7}$, (d) $(TTF)_3(BF_4)_2$, and (e) TTF·TNAP.
Observed peak (•••), simulated peak (——), and component peaks of simulation (···).

Table 2. Amount of (Donor)$^+$ and (Donor)^0 in the TTF and TTT complexes

	(Donor)$^+$ %	(Donor)^0 %
TTF·TCNQ	56±5	44±5
TTF·TNAP	55±5	45±5
TTF·$Br_{0.7}$	71±5	29±5
TTF·$I_{0.7}$	52±5	48±5
$(TTF)_3(BF_4)_2$	65±5	35±5
$(TTT)_2I_3$	49±5	51±5
(TTT)(TCNQ)$_2$	93±5	7±5

The errors were estimated from the *R*-maps obtained from the peak profile analysis.

valence TTF salts can be very satisfactorily reproduced by superimposing the S 2p peaks of TTF$^+$ and TTF^0.

From the intensity ratio of the component peaks which gives the best fit between the observed and calculated peak profiles ,we can estimate the relative amounts of TTF$^+$ and TTF^0 in each mixed-valence TTF salt. The results are listed in Table 2. In the case of TTF·$Br_{0.7}$, the relative amount of TTF$^+$ is determined to be 71 percent, which agrees well with the value that is expected from the chemical composition. The shape of the Br 3d peak of this salt coincides well with that of the Br 3d peak of KBr. Thus all XPS data consistently indicate that bromine atoms in TTF·$Br_{0.7}$ are completely in the state of Br^-. This is also consistent with the ESR data.[15] In the case of $(TTF)_3(BF_4)_2$, 67 percent of TTF molecules must be in the state of TTF$^+$ since each BF_4 group receives one electron from TTF. The relative amount of TTF$^+$ derived from the peak profile analysis is in good agreement with the above value. These examples do indicate the validity of our procedure of peak profile analysis. It is interesting to see that, in the case of TTF·$I_{0.7}$, the peak profile analysis gave the relative amount of TTF$^+$ significantly smaller than the value that is expected from the chemical composition. We noted also that the profile of the I $3d_{3/2}$ peak is appreciably different from that of KI, indicating that there are some iodine species which are different from I^-. Using the peak profile of I $3d_{3/2}$ of KI, we decomposed the I $3d_{3/2}$ peak observed of TTF·$I_{0.7}$ into the component corresponding to I^- and the one corresponding to the other iodine species which has less negative charge, possibly being in the state of I^0. The analysis of I $3d_{3/2}$ peak profile mentioned above gave the conclusion that about 79 percent of iodine atoms are in the state of I^-. If we assume that the remaining iodine atoms are in the neutral state, the relative amount of TTF$^+$ is expected to be 56 percent. This is in good agreement with the value obtained from the analysis of the S 2p peak profile. Seemingly an incomplete charge transfer is taking place in TTF·$I_{0.7}$. This conclusion is consistent also with the ESR data, which indicate that some unpaired spins are on iodine atoms.[15]

In the case of TTF·TCNQ, the analysis of the S 2p peak profile gave the relative amount of TTF$^+$ as 56 percent. From the analysis of the X-ray diffuse scattering, Comès *et al.*[5] and Kagoshima *et al.*[3] concluded that the degree of charge transfer from TTF to TCNQ is to be 59 percent. The relative amount of TTF$^+$ determined by the analysis of the S 2p peak profile is in good agreement with the above conclusion. The analysis of the S 2p peak profile gives almost same degree of charge transfer for TTF·TNAP.

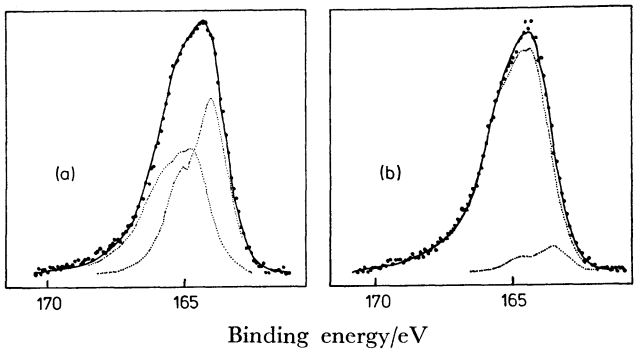

Fig. 6. S 2p peaks in the XPS spectra of (a) $(TTT)_2I_3$ and (b) (TTT)(TCNQ)$_2$.
Observed peak (•••), simulated peak (——), and component peaks of simulation (···).

The same procedure was taken for the analysis of S 2p peak profiles of TTT salts, using the S 2p peak profile of TTT and that of $(TTT)^+\cdot(ClO_4)^-$ as the standard peak profiles for TTT^0 and TTT$^+$ respectively. Results are shown in Fig. 6 and Table 2. In $(TTT)_2I_3$, iodine is known to exist as I_3^-.[27,28] Thus one should expect that a half of TTT molecules are in the ionized state. The result obtained by the analysis of the S 2p peak profile agrees with the above expectation. According to the analysis of the S 2p peak profile, almost all TTT molecules are in the ionized state in (TTT)(TCNQ)$_2$. If this is the case, a half of TCNQ molecules are in the state of $TCNQ^-$ and the remaining half are in the state of TCNQ^0. The shape of the N ls peak of this material is the same as those of the TCNQ complex salts where 50 percent of TCNQ molecules are in the ionized state, hence it is consistent with the conclusion obtained from the S 2p peak.

As we have mentioned, we treated the separation of the two component peaks as an adjustable parameter. This is because the shifts of the peaks associated with neutral molecules and ions are not necessarily the same for all TTF salts (or TTT salts), so that their separation could vary more or less from salt to salt. The relative separation of the component peaks obtained from the peak profile analysis was 0.9 eV for TTF·$Br_{0.7}$ and $(TTF)_3(BF_4)_2$, 1.0 eV for TTF·$I_{0.7}$, 1.2 eV for TTF·TCNQ, 1.4 eV for TTF·TNAP and 0.7 eV for the two TTT salts studied here. These values seem to be quite reasonable for the separation between the peaks due to TTF^0 and TTF$^+$ (or between those due to TTT^0 and TTT$^+$), but it is not possible to carry out at the present stage a quantitative discussion on the difference of the peak separation obtained for different salts.

The results described above show that observed S 2p peak profiles of TTF and TTT salts can be well reproduced by superimposing the standard peak profile characteristic of the neutral molecule and that of the

ion with an appropriate intensity ratio, and by this peak profile simulation, we can determine the ratio of neutral molecules and ions (or the degree of charge transfer).

As we have already mentioned, the situations are rather complicated in the case of the N ls peaks of TTF·TCNQ and TCNQ complex salts. The N ls peak profile of TTF·TCNQ, shown in Fig. 3, cannot be reproduced by superimposing the N ls peak profile observed of TCNQ and that of K·TCNQ with the intensity ratio that is expected from the degree of charge transfer. Almost same N ls peak profile is observed for $[(C_6H_5)_3PCH_3]^+(TCNQ)_2^-$ and other TCNQ complex salts which formally contain $TCNQ^-$ and $TCNQ^0$ with 1:1 mole ratio. In this respect, $Cu^+(TCNQ)_2^-$ is an exception. In this case, the observed N ls peak can be almost exactly reproduced by superimposing the N ls peak profile of $TCNQ^0$ and that of $TCNQ^-$ with the intensity ratio corresponding to the 1:1 mole ratio.[29] Unfortunately, the crystal structure of $Cu(TCNQ)_2$ is not known so far, but the arrangement of $TCNQ^0$ and $TCNQ^-$ in this salt is likely to be quite different from those in other TCNQ complex salts since $Cu(TCNQ)_2$ does not exhibit the absorption band which is characteristic of the charge transfer between $TCNQ^-$ and $TCNQ^0$.

TTF·TCNQ is a metal-like conductor, and conduction electrons (or holes) might be delocalized along the TTF stack as well as along the TCNQ stack. In spite of this delocalization of conduction electrons, the S 2p spectrum of TTF·TCNQ can be well explained as the superposition of the peak due to TTF neutral molecules and that due to TTF^+ ions. This fact may suggest that each TTF molecule in TTF·TCNQ can be regarded to be either in the state of TTF^+ or in the state of TTF^0 within the characteristic time scale of photoionization by X-ray. On the other hand, the N ls peak profile cannot be reproduced by the superposition of the peaks due to $TCNQ^0$ and $TCNQ^-$. The delocalization of conduction electrons along the TCNQ stack is not likely to be the origin of this phenomenon, since almost the same peak profile is observed also in many TCNQ complex salts which are not metal-like conductors, but are semiconductors of relatively low conductivity. Ritsko *et al.* suggested that the N ls peak profile of TTF·TCNQ could be understood in terms of the Hush's model[30] for the mixed-valence two-site system, by considering the local delocalization of valence electrons among neighboring TCNQ ions and molecules.[14] But, if this is the case, it is not easy to understand why the same mechanism does not work in the case of the S 2p spectra of TTF salts while a strong charge-transfer interaction is also taking place between TTF^0 and TTF^+.

As we have mentioned, in the N ls spectra of TCNQ salts, the relative intensity of the satellite band varies depending on the charge-transfer interaction between $TCNQ^-$ ions or between $TCNQ^0$ and $TCNQ^-$. Thus, one cannot expect anyway that the observed N ls peak profile of a TCNQ complex salt will be exactly reproduced by simply superimposing the N ls peaks of TCNQ and $K^+\cdot(TCNQ)^-$. Therefore, it is possible that each TCNQ molecule in a mixed-valence TCNQ stack can be regarded to be either in the state of $TCNQ^-$ or in that of $TCNQ^0$ as in the case of TTF molecules in a mixed-valence TTF stack, disregarding the delocalization of valence electrons, within the characteristic time scale of photoionization by X-ray, and the failure of the analysis of N ls peak profile is entirely due to the disturbing effect of the strong shake-up satellite.

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