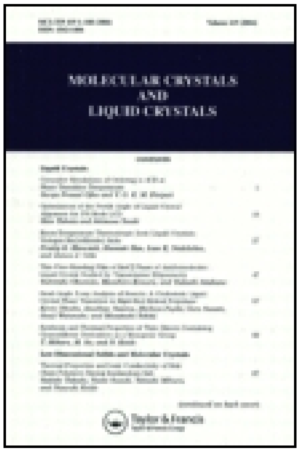

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Electronic Properties of 3,3′,5,5′-Tetramethyl-Benzidine Complexes with TCNQ Derivatives

Kenichi Imaeda [a] , Toshiaki Enoki [a] , Hiroo Inokuchi [a] & Gunzi Saito [b]
[a] Institute for Molecular Science, Okazaki 444, Japan
[b] Institute for Solid State Physics, The University of Tokyo, Roppongi, Minato-Ku, Tokyo, 106, Japan

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Electronic Properties of 3,3′,5,5′-Tetramethyl-Benzidine Complexes with TCNQ Derivatives

KENICHI IMAEDA, TOSHIAKI ENOKI and HIROO INOKUCHI
Institute for Molecular Science, Okazaki 444, Japan

and

GUNZI SAITO
Institute for Solid State Physics, The University of Tokyo, Roppongi, Minato-ku, Tokyo 106, Japan

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The electronic properties of the charge transfer complexes of 3,3′,5,5′-tetramethylbenzidine (33′55′TMB) with five TCNQ derivatives (F_4TCNQ, FTCNQ, TCNQ, Me_2TCNQ and $(MeO)_2$TCNQ) were investigated by electrical conductivities and electronic spectra measurements. 33′55′TMB-FTCNQ and 33′55′TMB-TCNQ showed the relatively low resistivities. Two charge transfer bands were observed in the electronic spectra of these complexes. From the correlation between the observed first charge transfer band and the estimated one, it was found that FTCNQ and TCNQ complexes were in the intermediate state between ionic and non-ionic states. The relatively low resistivities of FTCNQ and TCNQ complexes among the benzidine complexes were confirmed to be caused by partial charge transfer.

Keywords: benzidine complexes, charge transfer complexes, solid state properties, organic metals, electrical conductivities, electronic spectra

INTRODUCTION

It has been established that most of charge transfer complexes of various aromatic diamines are mainly classified into two groups, ionic and non-ionic complexes.[1,2] Ionic complexes generally exibit higher conductivities than non-ionic ones. Scott et al. have reported that 1,6-diaminopyrene-TCNQ complex shows a high conductivity $\sigma_{RT} = 2\ \Omega^{-1}\ \text{cm}^{-1}$ as a compressed pellet.[3] In the studies of a series of benzidine complexes, Ueda et al. found a high conductivity $\sigma_{RT} = 0.36\ \Omega^{-1}\ \text{cm}^{-1}$ on a single crystal of 2,7-bis(dimethylamino)-tetrahydropyrene-TCNQ complex.[4]

The requirements for organic metals have been proposed through many efforts to make highly conductive complexes.[5,6] One of them is that the complex has incomplete charge transfer to generate charge carriers. A degree of charge transfer is ruled mainly by the difference ($I_p - E_A$) between ionization potential (I_p) of a donor and electron affinity (E_A) of an acceptor and Madelung energy in a crystal. Ionic complexes have small values of ($I_p - E_A$), while non-ionic complexes have large ones. For making a metallic complex, it is desirable that the value of ($I_p - E_A$) ranges in a subtle region between the values in ionic and non-ionic complexes. The molecular structure of 3,3′,5,5′-tetramethyl-benzidine (33′55′TMB) used in the present work is shown in Figure 1. It is a strong donor molecule with $I_p \sim 6.8$ eV due to electron repelling two amino and four methyl groups. Therefore, 33′55′TMB is expected to form incomplete charge transfer complex in use of an acceptor with a suitable E_A. Another requirements are that a donor and/or an acceptor are planar and the complex has a segregated column structure. Judging from the fact that many of the TCNQ complexes form segregated stacks and indicate metallic conductivities, we choose five TCNQ derivatives as acceptors with different E_A in order to find complexes with an incomplete charge transfer. These are tetrafluoro-TCNQ (F_4TCNQ), fluoro-TCNQ (FTCNQ), TCNQ, 2,5-dimethyl-TCNQ (Me_2TCNQ) and 2,5-dimethoxy-TCNQ ($(MeO)_2$TCNQ).

In this work, we report electrical conductivities and electronic spectra of five charge transfer complexes of 33′55′TMB with TCNQ derivatives and discuss the relationship between the electrical conductivity and ionicity of the complex.

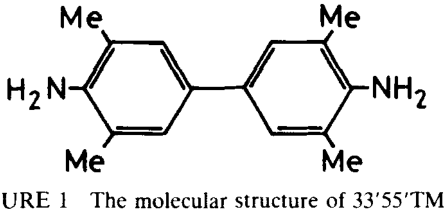

FIGURE 1 The molecular structure of 33′55′TMB.

EXPERIMENTAL

The complexes of 33′55′TMB with FTCNQ, TCNQ, Me_2TCNQ and $(MeO)_2$TCNQ were obtained as single crystals by a diffusion method with acetonitrile as a solvent. On the contrary, F_4TCNQ complex was obtained as polycrystalline powder using a cooling method by mixing hot acetonitrile solution of each component with the stoichiometric amounts. The compositions of the complexes were determined by elemental analysis.

The electrical conductivity was measured along the long axis of a crystal (except the F_4TCNQ complex as a compressed pellet) by a two probe method between about 110 K and room temperature with a Keithley 616 electrometer. The electrical contacts were achieved using silver paste. The electronic absorption spectra of the KBr tablet samples and the dichloromethane solution were measured with a Cary 17 spectrophotometer. The vibrational spectra of the KBr tablet samples were measured with a JEOL JIR-10 fourier-transform IR spectrophotometer.

RESULTS AND DISCUSSION

The electron affinity E_A of the acceptors and the color, shape and composition of 33′55′TMB complexes are listed in Table I. The activities of the acceptors increase in the order from $(MeO)_2$TCNQ to

TABLE I

Properties and electrical resistivities of 33′55′TMB complexes

X in 33′55′TMB-X	E_A[a] (eV)	Color and Shape	Composition (D:A)	ρ_{RT} (Ωcm)	ϵ_a (eV)
F_4TCNQ	3.15	purple powder	1:1	2.3×10^5	0.45
FTCNQ	2.92	black needle	1:1	4.6×10^2	0.22
TCNQ	2.83	greenish black needle	1:1	3.6×10^3	0.28 0.20
Me_2TCNQ	2.74	greenish black rod	1:1	8.8×10^6	0.40
$(MeO)_2$TCNQ	2.56	greenish black needle	1:1	1.1×10^7	0.46

[a] Reference 7.

F_4TCNQ. As for the complex formation, all of 33'55'TMB complexes have 1:1 stoichiometry.

The electrical resistivity at room temperature ρ_{RT} and activation energy ϵ_a of the complexes are also summarized in Table I. $(MeO)_2$TCNQ, Me_2TCNQ and F_4TCNQ complexes exhibit high resistivites, $10^7 \sim 10^5$ Ωcm, while FTCNQ and TCNQ complexes fairly low resistivities 4.6×10^2 and 3.6×10^3 Ωcm, respectively. The temperature dependence of the resistivity for the five complexes is shown in Figure 2. $(MeO)_2$TCNQ, Me_2TCNQ and F_4TCNQ complexes show simple semiconductive behaviors with ϵ_a of 0.46, 0.40 and 0.45 eV, respectively. On the other hand, FTCNQ and TCNQ complexes do not show a simple linear dependence in a logρ vs. 1/T plot and have lower ϵ_a than the other complexes. FTCNQ complex shows a semiconductive behavior with ϵ_a = 0.22 eV below 250 K, but the resistivity has an abrupt change at 250 K and a more gradual decrease above 250 K. In the case of TCNQ complex, ϵ_a changes in three steps, at two low temperature ones of which ϵ_a = 0.20 eV below 180 K and ϵ_a = 0.28 eV between 180 and 270 K. Then, the resistivity

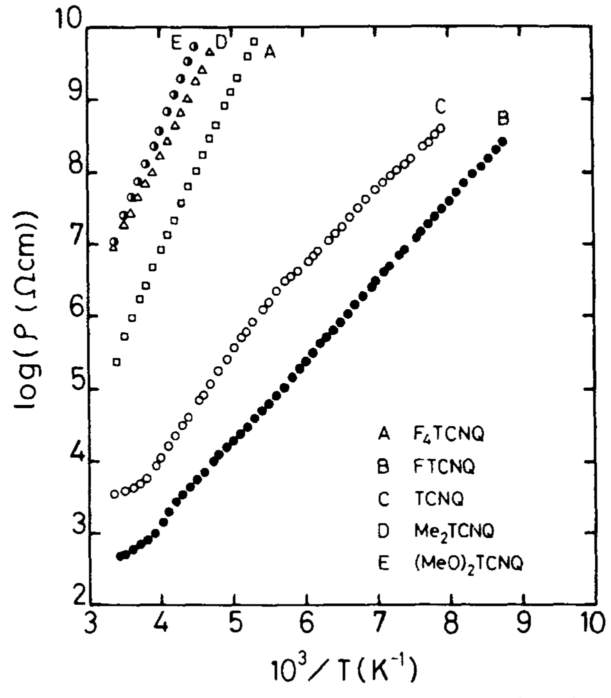

FIGURE 2 The temperature dependence of the resistivity of the 33'55'TMB complexes with the five TCNQ derivatives.

begins to decrease slowly above 270 K, which is similar to FTCNQ complex. These anomalies around 270 K and 180 K for TCNQ complex and 250 K for FTCNQ complex might be considered to be associated with some phase transitions.

The electronic spectra of the five 33'55'TMB complexes are shown in Figure 3. The two absorption bands, which are not observed in

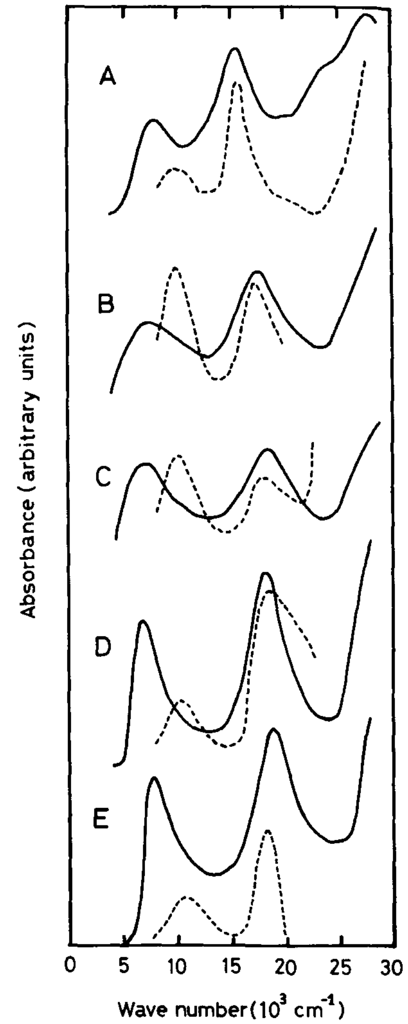

FIGURE 3 The electronic spectra of the 33'55'TMB complexes. The solid lines present the spectra in the KBr tablet samples, while the dash lines in CH_2Cl_2 solution, *A*, *B*, *C*, *D* and *E* denote the complexes with F_4TCNQ, FTCNQ, TCNQ, Me_2TCNQ and $(MeO)_2$TCNQ, respectively.

the spectra of each donor or acceptor component, are newly observed both in the solid state (KBr tablet) and dichloromethane solution. The first absorption band is located at 6900 ~ 7900 cm^{-1} in the solid and at 9800 ~ 10900 cm^{-1} in the solution, while the second one at 15500 ~ 19000 cm^{-1} in the solid and at 15700 ~ 18600 cm^{-1} in the solution. Table II summarizes the two absorption bands of the complexes. The first absorption band in the solid is shifted 1900 ~ 3400 cm^{-1} to lower energy region as compared with that in the solution and the second one almost does not change. This red-shift value is about the same to the shift in other benzidine complexes,[2,8] but a little larger than the shift in a typical CT complex (500 ~ 1000 cm^{-1}).[9] The difference between the first absorption band and the second absorption band in the solution is 5900, 7200, 7800, 8300 and 7500 cm^{-1} for F_4TCNQ, FTCNQ, TCNQ, Me_2TCNQ and $(MeO)_2$TCNQ complexes, respectively. Judging from the fact that they have about the same energy difference except F_4TCNQ complex, the first absorption band is assigned to the charge transfer from the highest occupied molecular orbital (HOMO) of 33′55′TMB to the lowest unoccupied molecular orbital (LUMO) of acceptor, while the second one to that from the second HOMO of 33′55′TMB to the LUMO of acceptor.[8] As for the assignment of the second absorption band, there is another possibility that it is the local excitation (LE) band of TCNQ derivative molecules.[10,11] Accordingly, the reason why the first charge transfer (CT) band shows a red-shift and the second one does not shift is considered that the former is easy to be affected by an environment, where a polarization energy for the solid and a solvation energy for the solution modify the electronic state, while the latter is difficult.

The preliminary X-ray diffraction study presented that 33′55′TMB-TCNQ crystal was triclinic with a space group $P\bar{1}$ and lattice param-

TABLE II

Absorption bands of 33′55′TMB complexes

X in 33′55′TMB-X	solid (KBr) 10^3 cm^{-1} 1st	solid (KBr) 10^3 cm^{-1} 2nd	soln (CH_2Cl_2) 10^3 cm^{-1} 1st	soln (CH_2Cl_2) 10^3 cm^{-1} 2nd
F_4TCNQ	7.9	15.5	9.8	15.7
FTCNQ	7.4	17.5	9.9	17.1
TCNQ	7.2	18.4	10.2	18.0
Me_2TCNQ	6.9	18.4	10.3	18.6
$(MeO)_2$TCNQ	7.8	19.0	10.9	18.4

eters; $a = 8.105$ Å, $b = 12.373$ Å, $c = 6.702$ Å, $\alpha = 100.14°$, $\beta = 101.94°$, $\gamma = 91.39°$, $V = 646.0$ Å^3 and $Z = 1$. Since the first CT band was observed for the polarization parallel to the c axis in the reflection spectrum of 33′55′TMB-$(MeO)_2$TCNQ crystal which is isostructural to the TCNQ complex, the direction of the donor-acceptor stack must be parallel to the c axis. These facts imply that 33′55′TMB complexes in this work have alternating stack structures.

The charge transfer absorption energy ($h\nu_{CT}$) in a non-ionic complex with 1:1 stoichiometry and an alternating stack structure can be expressed by the following equation:[12,13]

$$h\nu_{CT}(D \cdot A) = I_p(D) - E_A(A) - C(D \cdot A), \qquad (1)$$

where D is donor, A is acceptor and $C(D \cdot A)$ is an electrostatic Coulomb energy between a donor and an acceptor. The value of $h\nu_{CT}$ is approximately estimated from the experimental quantities using eq. (1) as follows:

$$\begin{aligned} &h\nu_{CT}(\text{est}) \\ &= h\nu_{CT}(D \cdot TNB) + h\nu_{CT}(\text{pyrene} \cdot A) - h\nu_{CT}(\text{pyrene} \cdot \text{TNB}) \\ &= I_p(D) - E_A(A) - C(D \cdot \text{TNB}) - C(\text{pyrene} \cdot A) + C(\text{pyrene} \cdot \text{TNB}), \quad (2) \end{aligned}$$

where TNB indicates s-trinitrobenzene. In eq. (2), TNB and pyrene are used as references. The observed electronic spectra give $h\nu_{CT}$ values: $h\nu_{CT}$(33′55′TMB · TNB) = 18200 cm^{-1}, $h\nu_{CT}$(pyrene · F_4TCNQ) = 10500 cm^{-1} is preceded by $h\nu_{CT}$(pyrene · TNB) = 22200 cm^{-1}, $h\nu_{CT}$(pyrene · FTCNQ) = 12400 cm^{-1}, $h\nu_{CT}$(pyrene · TCNQ) = 13000 cm^{-1}, $h\nu_{CT}$(pyrene · Me_2TCNQ) = 13800 cm^{-1} and $h\nu_{CT}$(pyrene · $(MeO)_2$TCNQ) = 15300 cm^{-1}. Thus $h\nu_{CT}$(est) of each complex is estimated as 6500, 8400, 9000, 9800 or 11300 cm^{-1} for F_4TCNQ, FTCNQ, TCNQ, Me_2TCNQ or $(MeO)_2$TCNQ complex, respectively. Figure 4 shows the correlation between the observed $h\nu_{CT}$ ($h\nu_{CT}$(obsd)) of the first CT band both in the solid and solution and h_{CT}(est). If the Coulomb term C in eq. (2) is assumed to be constant and independent of a sort of TCNQ derivatives for the non-ionic complex, $h\nu_{CT}$(obsd) should show a linear dependence with a 45° slope against $h\nu_{CT}$(est) because I_p is constant in the present work. Me_2TCNQ and $(MeO)_2$TCNQ complexes are nearly situated on the straight line, while TCNQ, FTCNQ and F_4TCNQ complexes deviate

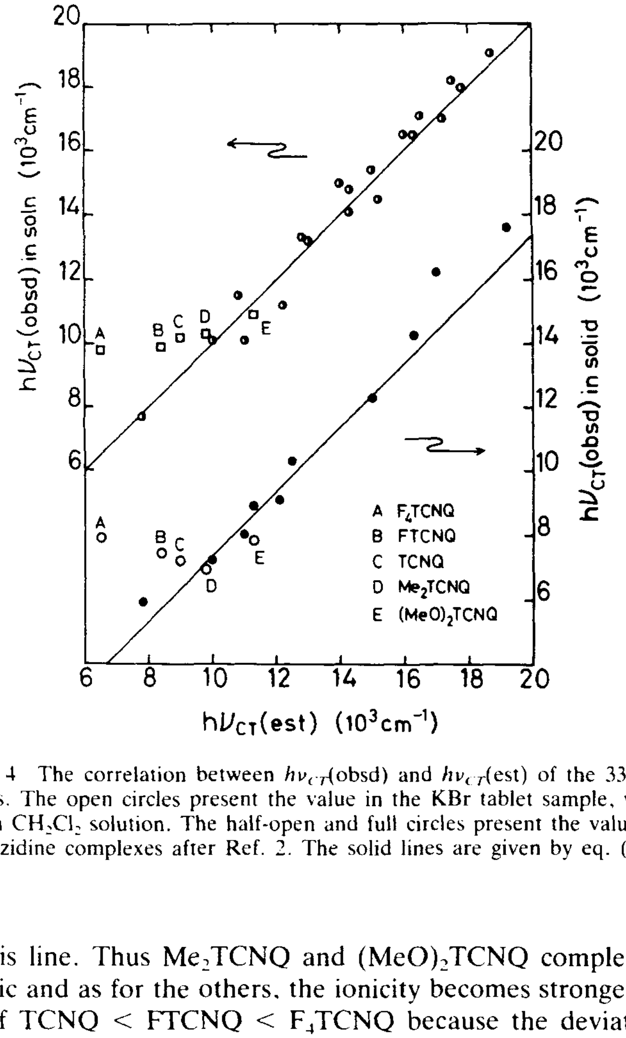

FIGURE 4 The correlation between $h\nu_{CT}$(obsd) and $h\nu_{CT}$(est) of the 33′55′TMB complexes. The open circles present the value in the KBr tablet sample, while the squares in CH_2Cl_2 solution. The half-open and full circles present the values of the other benzidine complexes after Ref. 2. The solid lines are given by eq. (1) in the text.

from this line. Thus Me_2TCNQ and $(MeO)_2$TCNQ complexes are non-ionic and as for the others, the ionicity becomes stronger in the order of TCNQ < FTCNQ < F_4TCNQ because the deviation increases in the order, which is in accordance with the order of the electron affinity of these acceptors shown in Table I. Furthermore, the tendency that the nitrile streching vibrational frequencies in FT-IR spectra of 33′55′TMB complexes gradually approach to those of alkali metal salts in the order from $(MeO)_2$TCNQ to F_4TCNQ is in qualititative agreement with the results of the electronic spectra.

Figure 5 shows the correlation between (I_p − E_A) and logρ_{RT} or ϵ_a of 33′55′TMB complexes. FTCNQ and TCNQ complexes show the relatively low resistivities and lower activation energies. This result is reasonable with the fact that they are the complexes with partial CT on the basis of the intermediate ionicity between ionic and

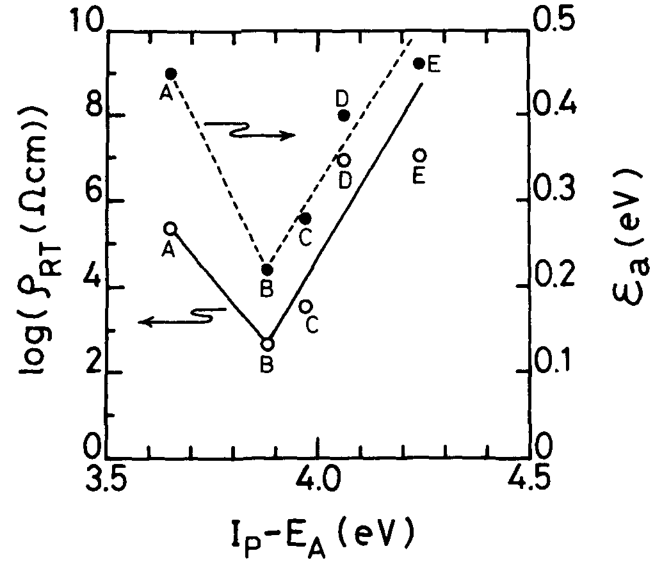

FIGURE 5 The correlation between ($I_p - E_A$) and $\log\rho_{RT}$ or ϵ_a of the 33′55′TMB complexes. ($I_p - E_A$) values are estimated using E_A of acceptors shown in Table I assuming that I_p of 33′55′TMB is ~6.8 eV. *A*, *B*, *C*, *D* and *E* denote the complexes with F_4TCNQ, FTCNQ, TCNQ, Me_2TCNQ and $(MeO)_2$TCNQ, respectively. The solid and dash lines are drawn to guide the eye.

non-ionic states. Though 33′55′TMB complexes did not have a segregated stack structure with many regrets, it is suggestive that partial *CT* brings about fairly good conduction, in order to find a clue to organic metals based on benzidine complexes.

SUMMARY

The electronic properties of 33′55′TMB complexes with F_4TCNQ, FTCNQ, TCNQ, Me_2TCNQ and $(MeO)_2$TCNQ have been investigated by means of electrical conductivities and electronic spectra measurements. FTCNQ and TCNQ complexes show the relatively low resistivities 4.6×10^2 and 3.6×10^3 Ωcm at room temperature, respectively. The two *CT* bands are observed in the electronic spectra of the five complexes. The correlation between the observed first *CT* band and estimated one suggests that FTCNQ and TCNQ complexes are in the intermediate state between ionic and non-ionic states. Accordingly, the relatively low resistivities of FTCNQ and TCNQ complexes are considered to be caused by partial *CT*. Though these complexes do not show a metallic conductivity in spite of partial *CT* because of their alternating stack structures, it is concluded that partial *CT* is a significant requirement for making *CT* complexes with a low resistivity. An important finding in our study is that an ionicity of a complex is able to be controlled by changing an activity of an acceptor and the FTCNQ and TCNQ complexes are in between an ionic state and a neutral state. This situation suggests a possibility of a neutral-ionic (N—I) transition in 33'55'TMB-FTCNQ and 33'55'TMB-TCNQ, similar to TTF-p-chloranil which was found to take place an N—I transition by Torrance et al.[13,14] An N—I transition in this system is not observed yet by preliminary experiment. This suggests that an N—I transition is caused not only by the electronic effect but also by the structural factor. The application of pressure leading to a structural modification may induce an N—I transition even in this system.

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