Polarized Absorption and Reflection Spectra of the Single Crystals of 11,11,12,12-Tetracyano-2,6-naphthoquinodimethan (TNAP) Complexes

Kyuya YAKUSHI, Yoshiyuki SATO, Isao IKEMOTO,*,† and Haruo KURODA

Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Bunkyo-yu, Tokyo 113

† *Research Center for Spectrochemistry, Faculty of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113*

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The electronic absorption spectra of 2,6-bis(dicyanomethylene)-2,6-dihydronaphthalene (11,11,12,12-tetracyano-2,6-naphthoquinodimethan; TNAP) and its anion radical ($TNAP^-$) were studied. The absorption bands of the solution spectra of $TNAP^0$ and $TNAP^-$ were successfully assigned to the electronic transitions which were calculated by the use of molecular orbital method. The polarized absorption and reflection spectra were measured on the single crystals of Na·TNAP and (methyltriphenylphosphonium)$(TNAP)_2$ [(MTPP)$(TNAP)_2$]. The low-lying electronic excitations of these complexes are quite similar to those of the corresponding tetracyanoquinodimethan (TCNQ) salts.

The discovery of the low-dimensional metallic behavior of organic charge-transfer salts such as tetrathiafulvalene–tetracyanoquinodimethan (TTF–TCNQ)[1] strongly stimulated research concerning the physical properties of related organic charge-transfer salts and the synthesis of new organic electron donors and acceptors.

2,6-Bis(dicyanomethylene)-2,6-dihydronaphthalene (11,11,12,12-tetracyano-2,6-naphthoquinodimethan; TNAP) was synthesized by Diekmann *et al.* and shown to be a strong acceptor.[2] The simple salts of TNAP were found to have higher conductivities than the analogous TCNQ salts,[2] and HMTSF–TNAP (2,2'-bi[2,4-diselenabicyclo[3.3.0]octan-2-ylidene]–TNAP) was found to have very high electrical conductivity at room temperature.[3] For understanding the electronic behaviors of those TNAP complexes, it is necessary to accumulate the data concerning the electronic structures of TNAP complexes.

In the present study, we have investigated the polarized absorption and reflection spectra of the single crystals of the simple salt, Na·TNAP, and the complex salt, (methyltriphenylphosphonium)$(TNAP)_2$ [(MTPP)$(TNAP)_2$].

Experimental

TNAP was synthesized by the procedures described in the literature[2,4,5] and purified by recrystallization from an acetonitrile solution. The complexes, Na·TNAP and (MTPP)$(TNAP)_2$ were obtained according to the method described in the literature.[2,5]

Polarized absorption and reflection spectra were measured on very small single crystals by use of the microspectrophotometric apparatuses for the transmission and reflection spectroscopies. The details of those apparatuses and the procedure of measurement have been described elsewhere.[6,7] All spectra were obtained at room temperature.

Absorption spectra of solutions were measured using a Hitachi EPS-3 spectrometer.

Results and Discussion

Electronic Transitions of TNAP Molecule and $TNAP^-$ Ion. In order to interpret the crystal spectra of TNAP complexes, it is of essential significance to know the electronic transitions in TNAP molecule and $TNAP^-$ ion. In Fig. 1, we show the solution spectra of $TNAP^0$ and $TNAP^-$, obtained from acetonitrile solutions of TNAP and K·TNAP. The observed wave numbers, molar extinction coefficients, and oscillator strengths of absorption bands are listed in Table 1. To find out the assignments of the observed absorption bands, we carried out SCF-MO-CI calculations on the π electron systems of the molecule and ion of TNAP.[8] The results are also included in Table 1. The predicted transitions are indicated in Fig. 1, with the vertical lines, the length of which is proportional to the predicted oscillator strengths, the directions of transition moment being shown with an arrow.

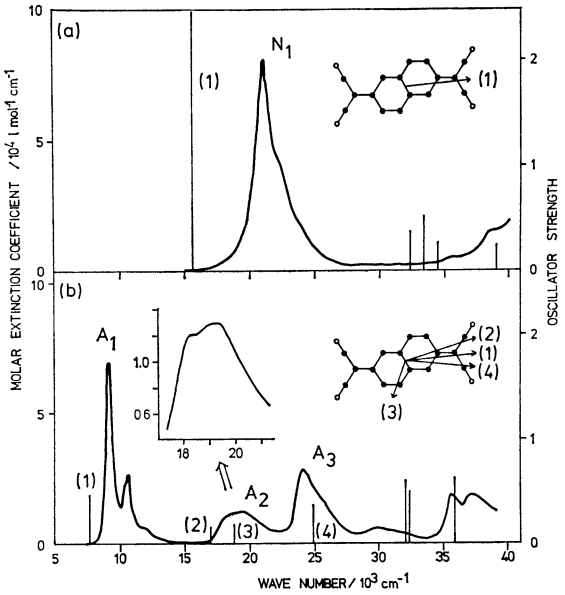

Fig. 1. The solution spectra of (a) TNAP molecule and (b) $TNAP^-$ ion in the acetonitrile solutions. The vertical lines represent the results of the SCF-MO-CI calculations. The arrows represent the directions of the transition moments.

In the solution spectrum of $TNAP^0$, there appears a strong absorption band at 21.1×10^3 cm^{-1} which is completely isolated from other weak absorption bands. The molecular orbital calculation predicted that the transition (1) had a strong oscillator strength (2.47) and was separated far from other transitions as shown in Fig. 1a. Therefore, the absorption band, N_1, is unambiguously assigned to the transition (1).

Table 1. Wave numbers, molar absorption coefficients, and oscillator strengths of local excitation bands of $TNAP^0$ and $TNAP^-$

	Obsd				Calcd			
	Transition	$\tilde{\nu}$[a] / 10^3 cm^{-1}	ε[b] / l mol^{-1} cm^{-1}	f[c]	Transition	$\tilde{\nu}$[d] / 10^3 cm^{-1}	f[e]	Dominant[f] configuration
$TNAP^0$	N_1	21.1	79600	0.94	(1)	16.6	0.82	$6a_u \leftarrow 5b_g$
$TNAP^-$	A_1	9.0	84400	0.38	(1)	7.7	0.16	$6a_u \leftarrow 5b_g$ and vibrational structures
		10.6	30400					
		11.8	7500					
	A_2	18.8	14200	0.18	(2)	17.0	0.12	$6b_g \leftarrow 6a_u$
		19.3	15000		(3)	18.8		$7b_g \leftarrow 6a_u$
	A_3	23.9	32800	0.32	(4)	25.0	0.12	$8b_g \leftarrow 6a_u$

a) Wave numbers. b) Molar absorption coefficients. c) Oscillator strengths. d) Wave numbers. e) Oscillator strengths which are divided by 3 in order to compare them with the experimentally obtained values from the solution spectrum. f) The dominant configuration of the wave functions of the ground states in $TNAP^0$ and $TNAP^-$ ion are represented as follows respectively;

$TNAP^0$: $\Psi_0 = (1a_u)^2(1b_g)^2(2a_u)^2(3a_u)^2(2b_g)^2(3b_g)^2(4b_g)^2(4a_u)^2(5a_u)^2(5b_g)^2(6a_u)^0$,

$TNAP^-$: $\Psi_0 = (1a_u)^2(1b_g)^2(2a_u)^2(3a_u)^2(2b_g)^2(3b_g)^2(4b_g)^2(4a_u)^2(5a_u)^2(5b_g)^2(6a_u)^1(6b_g)^0(7a_u)^0(7b_g)^0(8b_g)^0$.

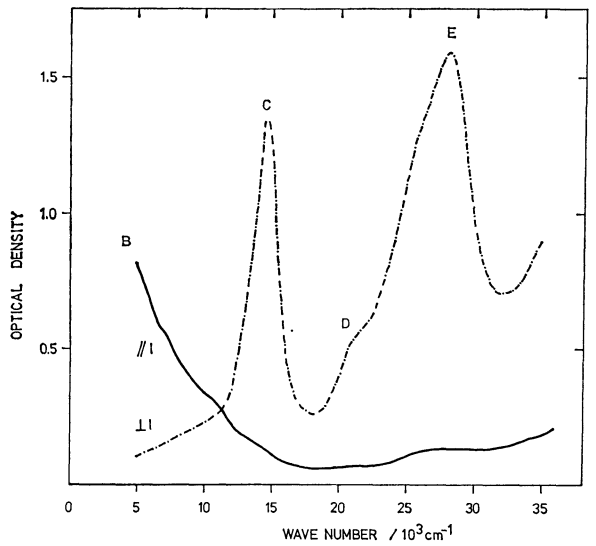

Fig. 2. Polarized absorption spectra of the single crystal of Na·TNAP.

The direction of the transition moment is almost parallel to the long axis of the molecule. The spectral features in this region are quite similar to those of $TCNQ^0$ except that the excitation energy of $TNAP^0$ is lower by about 3×10^3 cm^{-1} as compared with $TCNQ^0$.

The solution spectrum of $TNAP^-$ ion is more complicated than that of $TCNQ^-$ ion. We will denote the absorption bands as A_1, A_2, and A_3, respectively, in the order of increasing wave number, as shown in Fig. 1b. The structure of the band A_1 is similar to the vibrational structure of the absorption band of $TCNQ^-$ ion which has been assigned to the transition from the highest doubly occupied molecular orbital to the top-most singly-occupied molecular orbital. We can assign this band to the transition (1). The absorption band A_2 is broad and has a shoulder in the low wave number edge as shown in the inset of Fig. 1b. Probably it is composed of two electronic transitions. We will tentatively assign the band A_2 to the superimposition of the transitions (2) and (3). The band A_3 can be assigned to the transition (4) by comparing the observed energy and oscillator strength of this band with the calculated results.

Table 2. Wave numbers of absorption bands in the spectra of Na·TNAP

Absorption bands	$\tilde{\nu}$[a] / 10^3 cm^{-1}	Transition character
B	<5	CT: $(TNAP)^-(TNAP)^- \rightarrow (TNAP)^0(TNAP)^{2-}$
C	14.5	LE: A_1
D	21.0	LE: A_2
E	28.0	LE: A_3

a) Wave numbers.

Na·TNAP. Na·TNAP is expected to be a salt composed of Na^+ and $TNAP^-$. Light-green plate-like crystals of this complex can be obtained from the acetonitrile solution. Since the crystal structure has not been known, the absorption spectra of the crystal were observed with the light polarized parallel and perpendicular to the elongated axis ($//l$ and $\perp l$) of the crystal. The observed spectra are shown in Fig. 2. The wave numbers of the observed bands are listed in Table 2. The $//l$ spectrum exhibits a strong absorption band below 5×10^3 cm^{-1} (B). There is no absorption band in this region in $\perp l$ spectrum. Thus the absorption band (B) is completely polarized in the direction of the l-axis which is likely to be the stacking axis of $TNAP^-$. We cannot expect any local excitation band associated with an intramolecular transition of $TNAP^-$ in this region. Thus the observed absorption band (B) must be the one arising from the charge transfer (CT) between $TNAP^-$ ions.

In the region above 9×10^3 cm^{-1}, the $//l$ spectrum shows no absorption band although the $\perp l$ spectrum

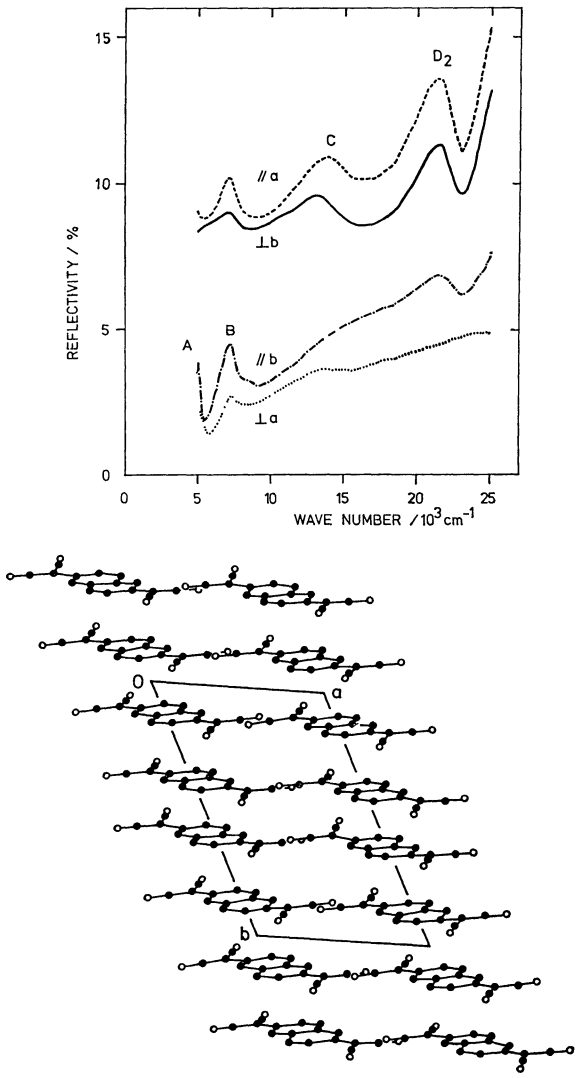

Fig. 3. Polarized reflection spectra of the single crystal of (MTPP)(TNAP)$_2$ measured on the (001) plane and the projection of TNAP molecules in the crystal onto (001) plane.

shows three absorption bands (C, D, and E). By comparing this $\perp l$ spectrum of Na·TNAP with the solution spectrum of TNAP$^-$, we can conclude that 14.5×10^3 (C), 21.0×10^3 (D), and 28.0×10^3 (E) cm^{-1} bands are the local-excitation bands corresponding to the 9—11.8×10^3 (A_1), 18.8—19.3×10^3 (A_2) and 23.9×10^3 (A_3) cm^{-1} bands in the solution spectrum of TNAP$^-$ ion, respectively. The relative intensity of the band D is very weak in comparison with the solution spectrum. It seems to be due to the difference of the direction of transition moment between the transition (2) and (3).

The local excitation bands C, D, and E are located at wave numbers higher by about 4—5×10^3 cm^{-1} as compared with the corresponding absorption bands of the solution spectrum of TNAP$^-$ ion. This is just the magnitude of the shift that is often found in the crystal where the intermolecular charge-transfer interaction is taking place between the constituent radical ions.[9]

(MTPP)(TNAP)$_2$. The crystal structure of this complex has been revealed by Sanz and Daly.[10] It is triclinic. In this crystal, TNAP molecules are arranged in groups of the four molecules which are almost parallel and equally spaced (3.30 Å) with each other. In other words, the crystal is composed of TNAP tetrads. The molecules between two consecutive tetrads are 3.46 Å apart. There is not significant difference in the molecular geometries of the four molecules in a tetrad.

The reflection spectra were measured on the (100) and (001) planes. On the (001) plane, the spectra were measured with the light polarizations, parallel to b and a axes (//b and //a) and perpendicular to b and a axes ($\perp$b and $\perp$a). On the (100) plane, the spectra were measured with the light polarizations parallel to b and c axes (//b and //c) and perpendicular to b and c axes ($\perp$b and $\perp$c). The observed reflection spectra are shown in Figs. 3 and 4 with the projections of TNAP molecules. The absorption spectra directly measured by the transmission method are shown in

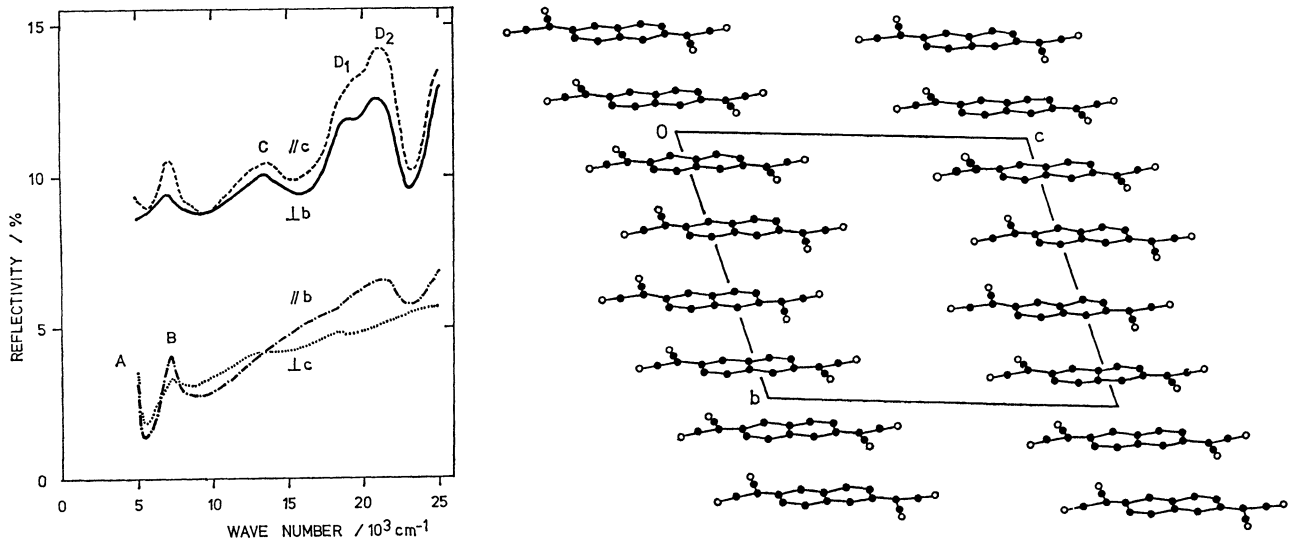

Fig. 4. Polarized reflection spectra of the single crystal of (MTPP)(TNAP)$_2$ measured on the (100) plane and the projection of TNAP molecules in the crystal onto (100) plane.

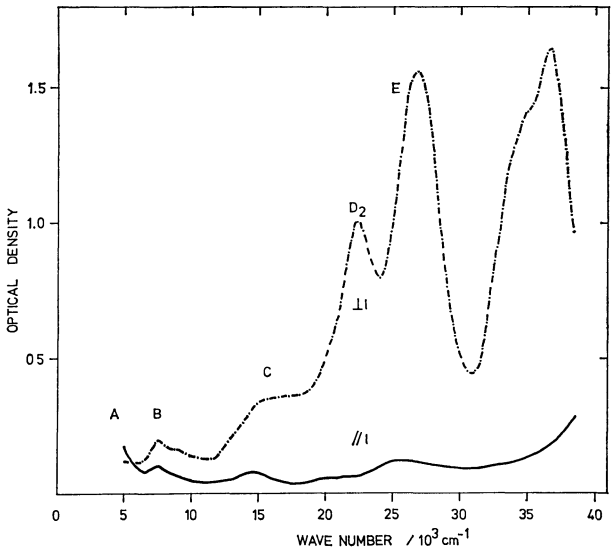

Fig. 5. Polarized absorption spectra of the single crystal of (MTPP)(TNAP)$_2$.

Fig. 5. Although we were not able to determine the observed crystallographic face directly, it is likely to be the (001) plane since it is in satisfactory agreement with the absorption spectra derived from the dispersion analysis of the reflection spectra obtained on the (001) crystal face. Therefore, we can consider that the spectra shown in Fig. 5 and the //a and ⊥a spectra. The wave numbers of the observed bands are listed in Table 3. The absorption spectra of this salt in the region lower than 17×10^3 cm^{-1} is quite similar to that of (MTPP)(TCNQ)$_2$ when we shift the spectrum of (MTPP)(TCNQ)$_2$ by about 3×10^3 cm^{-1} to higher wave number. The solution spectra of TNAP^0 and TNAP$^-$ are quite similar in nature with the spectra of TCNQ^0 and TCNQ$^-$, respectively, and the general feature of the crystal structure of (MTPP)(TNAP)$_2$ are almost the same as that of (MTPP)(TCNQ)$_2$. Therefore, we can interpret the electronic spectrum of (MTPP)(TNAP)$_2$ in analogy with that of (MTPP)-(TCNQ)$_2$. We have previously examined the temperature dependency of the reflection spectrum of (MTPP)(TCNQ)$_2$ and proposed an interpretation of the observed spectrum.[11] Using this result, we can assign the band A to the CT transition of the type TNAP^{0}TNAP$^-$→TNAP$^-$TNAP^0, the band B mainly to the local excitation of TNAP$^-$ (A_1) and the band C to the CT transition from the second highest occupied molecular orbital of TNAP$^-$ to the lowest unoccupied molecular orbital of TNAP^0, which appears with an increased intensity by borrowing the intensity from the strong lowest transition of TNAP^0.

Let us examine the transition in the region about 20×10^3 cm^{-1}. The absorption spectrum measured on the (001) plane shows one absorption band in this region. The reflection spectra of the (001) crystal face also shows only one dispersion at the corresponding region. However, the c-polarized reflection spectra in the (100) crystal face shows that another dispersion (D_1) is superimposed on the dispersion D_2 as shown in Fig. 4. This result means that the direction of the transition moment of D_1 band is different from that of D_2 band. Since the direction of the transition moment of D_2 is almost parallel to those of C and E, D_1 must be attributable to the local excitation band associated with the transition (3) of TNAP$^-$, whose transition moment was predicted to be different from other transitions by the molecular orbital calculation as illustrated in Fig. 1b.

The absorption band E seems to correspond to the superimposition of the lowest transition of TNAP^0 and the transition (4) of TNAP$^-$.

Table 3. Wave numbers of absorption bands derived from the dispersion analysis of the reflection spectra of (MTPP)(TNAP)$_2$

Absorption bands	$\tilde{\nu}$[a] / 10^3 cm^{-1}	Transition character
A	<5	(TNAP)^0(TNAP)$^-$ → (TNAP)$^-$(TNAP)^0
B	7.2, 8.5(sh)	LE : mainly A_1
C	15.0	CT : See the text
D_1	18.5	LE : A_2 (transition (3))
D_2	21.0	LE : A_2 (transition (2))
E	27.0	LE : A_3 and N_1

a) Wave numbers.

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