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Organic Charge Transfer Salts. II.[1] Emission Spectrum of an Organic Charge Transfer Salt, 2,4,6-Triphenylthiopyrylium-1,1,3,3-tetracyanopropenide

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The emission spectrum of an organic charge transfer salt, 2,4,6-triphenylthiopyrylium-1,1,3,3-tetracyanopropenide, was studied in solutions of various solvents as well as in the solid state. A charge transfer fluorescence was observed both in the solid state and in non-polar rigid solution at 77 K, but not in fluid solution. In rigid solution, as the polarity of solvent increases, the charge transfer fluorescence shows a blue shift of its maximum wavelength and a remarkable decrease in intensity, the phosphorescence of a dissociated cation appearing predominantly. The strong dependence of the emission spectrum on the solvent polarity was explained in terms of the dissociation of the salt and the insufficient reorientation of solvent molecules around the salt in the excited charge transfer state.

An organic salt in which a charge-transfer (CT) interaction is present between an anion and a cation, which we have called an organic CT salt, has a predominantly ionic ground state and an excited state consisting of two neutral radical species. A report was given[2] on the CT absorption spectra of some new organic salts consisting of a pyrylium or thiopyrylium cation and a polycyanoacid anion(Fig. 1). The CT absorption spectra of these salts in solution were found to be very solvent sensitive due to two factors. With an increase in solvent polarity (i) the intensity of the CT band decreases by the dissociation of the salt into component ions, and (ii) the CT absorption peak shows a remarkable blue shift, which can be explained by Kosower's theorem.[3–5]

Although extensive studies have been carried out on the absorption spectra of organic CT salts,[2–11] few have been made on the emission spectra.[12] It seems that the solvent effect on the emission spectrum has not yet been elucidated in a wide range of solvent polarity. Of the salts we prepared, 2,4,6-triphenylthiopyrylium (TPT, Fig. 1 (2))–1,1,3,3-tetracyanopropenide (TCP, Fig. 1 (5)) is fairly soluble in various solvents including non-polar ones such as toluene or 1,4-dioxane, and with this we could investigate the solvent effect of the emission spectrum of an organic CT salt in detail. In addition to the temperature dependence of the absorption spectrum of TPT–TCP, we have also examined the emission spectrum of this salt in the solid state and in solutions of various solvents. TPT–TCP in the solid state shows exclusively a CT fluorescence, the emission from the component ion being completely quenched. This is the first example of the CT fluorescence of an organic CT salt in a crystalline solid state. In rigid solution of non-polar solvent at 77 K, the salt also shows a CT fluorescence. The CT fluorescence at 77 K shows a remarkable solvent effect both in intensity and energy. These solvent effects should be understood in terms of the dissociation of the salt in rigid solution and the relaxation behavior of solvent molecules around the CT excited state. In contrast to the case of a rigid solution, TPT–TCP does not show a CT fluorescence when dissolved in fluid solution irrespective of the solvent.

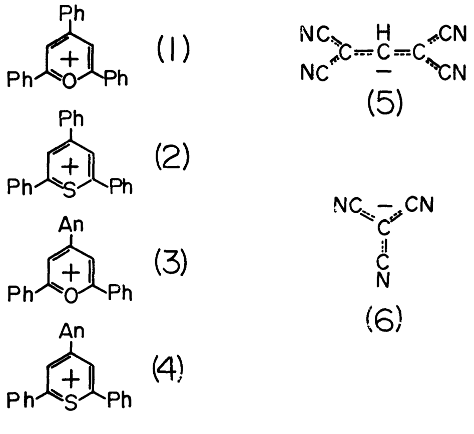

Fig. 1. (1) 2,4,6-triphenylpyrylium (TPP) cation, (2) 2,4,6-triphenylthiopyrylium (TPT) cation, (3) 4-anisyl-2,6-diphenylpyrylium (ADPP) cation, (4) 4-anisyl-2,6-diphenylthiopyrylium (ADPT) cation, (5) 1,1,3,3-tetracyanopropenide (TCP) anion, (6) tricyanomethanide (TCM) anion.

Experimental

The preparation of TPT–TCP and other salts used here have been reported.[2] For the measurement of the emission spectrum in the solid state, the microcrystalline sample was sealed in a pyrex tube (2 mm diameter) under vacuum. Each sample in solution having an appropriate concentration was degassed and sealed in a pyrex tube. All solvents used were purified according to the usual purification method.[13] Emission spectra were recorded on a Hitachi model MPF-3 spectrophotofluorometer equipped with a Xe excitation lamp and an R-446 photomultiplier tube, delayed emissions being measured with a delayed emission accessory including a cylindrical chopper to eliminate prompt emission. The spectra obtained were not corrected both for the excitation source and for the photomultiplier response. Phosphorescence lifetimes were estimated from the decay curves on an oscilloscope. Fluorescence lifetimes were measured by the pulse method with an N_2 gas laser excitation (337 nm, 5 nsec half-width). Absorption spectra were measured with a Hitachi EPS-3 UV spectrophotometer or a Cary model 14 spectrophotometer.

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Results and Discussion

Absorption Spectrum. The absorption spectrum of TPT-TCP in a chloroform solution and the diffuse reflectance spectrum of the salt in the solid state are shown in Figs. 2a and 2b, respectively. These spectra are compared with sodium–TCP and TPT–perchlorate salts in methanol solution and TPT–perchlorate salt in the solid state. The absorption spectrum of TPT–TCP in solution consists mainly of three bands with the maximum wavelength at 350, 390 and 595 nm (Fig. 2a). The 350 and 390 nm bands correspond to the sum of the absorptions of TCP anion and TPT cation, and are assigned to the locally excited (LE) absorption bands of the component ions of the salt. Another absorption band at 595 nm is assigned to an interionic CT band, since it does not appear either in sodium–TCP or TPT–perchlorate salts where a CT interaction is absent between the cation and the anion. In the solid state, the corresponding CT absorption band is observed near 540 nm (Fig. 2b).

In order to understand the low temperature emission spectrum, the absorption spectrum was studied at low temperatures. The CT band shows a considerable blue shift as the temperature is lowered. The absorption spectra of TPT–TCP in 2-methyltetrahydrofuran (2MTHF)–toluene (9 : 1) solution at various temperatures are shown in Fig. 3. At 77 K, the LE bands of the component ions become sharp, but show no shift in maximum wavelength as compared with that at room temperature. The CT absorption maximum, however, shows a blue shift of 45 nm at 227 K and 120 nm at 77 K from the position of this band at room temperature. A consiberable decrease in absorbance of the CT band occurs together with the blue shift. Such a shift was observed in dichloromethane solutions of some alkylpyridinium–halide salts by Brinen *et al.*,[12] but they did not discuss the reason for this. We conclude that the blue shift is due to the increase of solvent polarity at low temperatures.

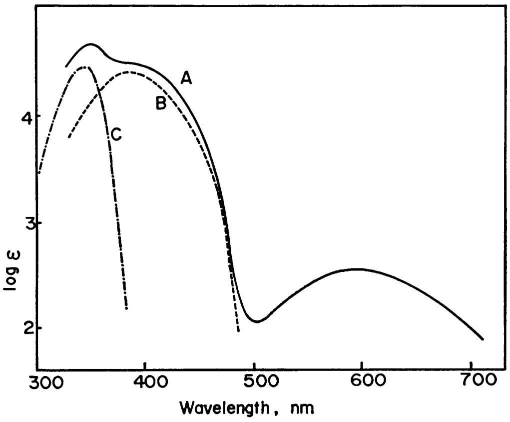

Fig. 2(a). Absorption spectra of TPT-TCP salt in chloroform solution and of its component ions.
(A) TPT-TCP in $CHCl_3$, (B) TPT-perchlorate in CH_3OH, (C) sodium-TCP in CH_3OH.

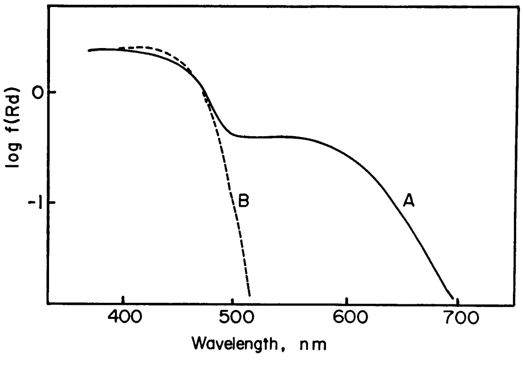

Fig. 2(b). Diffuse reflectance spectra of TPT-TCP and TPT-perchlorate salts in the solid state.
(A) TPT-TCP, (B) TPT-pcrchlorate.

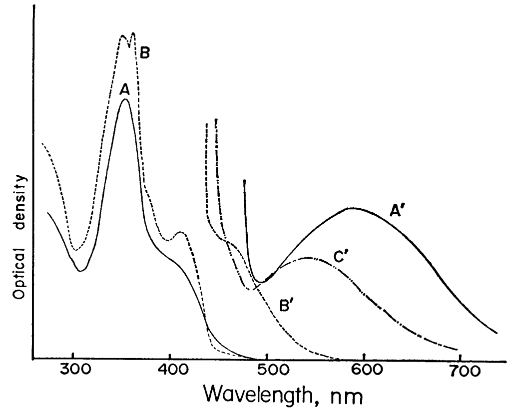

Fig. 3. Absorption spectra of TPT-TCP salt in 2MTHF-toluene (9 : 1) solution at various temperatures.
(A) 4.0×10^{-5} mol/l, room temperature, (A′) 2.0×10^{-3} mol/l, room temperature, (B) 4.0×10^{-5} mol/l, 77 K, (B′) 2.0×10^{-3} mol/l, 77 K, (C′) 2.0×10^{-3} mol/l, 223 K.

The maximum wavelength (λ_{max}) and the apparent molar extinction coefficients (ε_{app}) of the CT band of TPT-TCP in various solvents *at room temperature* are given in Table 1. With the increase of solvent polarity, the CT band shows a remarkable blue shift of λ_{max} and a decrease in ε_{app}. Since the energy of the CT band maximum shows a linear dependence on the

TABLE 1. SOLVENT EFEECT OF THE CT ABSORPTION BAND OF TPT-TCP AT ROOM TEMPERATURE

Solvent	D	Z-value (kcal/mol)	λ_{max} (nm)	ε_{app}
1,4-Dioxane	2.21	58.3	635	550
Toluene	2.38	55.4	660	525
Chloroform	4.70	63.2	595	370
Ethyl acetate	6.03	57.6	583	240
Acetic acid	6.15	79.2	510	180
2MTHF	7.0	65.0	585	220
Dichloromethane	8.9	64.2	575	100
1,2-Dichloroethane	10.37	62.7	568	70
Benzyl alcohol	13.6	—	—[a]	—
Isopropyl alcohol	16.3	76.3	—[a]	—

[a] The CT absorption band did not appear appreciably in this solvent.

Z-value of the solvent, or the empirical parameter of the solvent polarity,[3–5] the shift can be explained on the basis of Kosower's theorem. On the other hand, the decrease in ε_{app} is caused by the dissociation of an ion-pair, $D^-A^+ \rightarrow D^- + A^+$, where D^-A^+ is an ion-pair and D^- and A^+ are dissociated component ions. ε_{app} is more closely related to the dielectric constant (D) of solvent than to the Z-value (Table 1). The CT absorption peak is not conspicuous in the solvents with $D > 10$ at room temperature, probably due to the almost complete dissociation of the ion-pair. Thus, the temperature dependence of the CT band shown in Fig. 3 can be understood phenomenologically in terms of the change in the solvent polarity with temperature.

It is known that the polarity of solvent increases with the lowering of temperature because of the enhanced orientation of the solvent dipole. Furutsuka *et al.* reported that the value of D of 2MTHF at 298, 223, just above the glass transition temperature (108 K), and below 108 K are 7.0, 9.0, 18.0, and 3.5, respectively.[14] Thus, the dielectric constant increases with the lowering of temperature down to the glass transition temperature. Even near the glass transition temperature of 2MTHF–toluene (9 : 1), the solvent molecules around the salt are expected to be in a well-oriented state. Although the D value of solvent is very small below glass transition temperature, the local solvent orientation around the salt may be kept even in the frozen state. The Z-value of the solvent, therefore, may increase with the lowering of temperature, and may not decrease even in a glass. From the result shown in Fig. 3, the Z-value of 2MTHF–toluene (9 : 1) at room temperature, 223, and 77 K can be estimated to be about 64, 72, and 88 kcal/mol. Thus the blue shift and the decrease of absorbance of the CT band can be accounted for by the increase of solvent polarity in a low temperature region.

Emission Spectrum in the Cyrstalline State. Although sodium–TCP gives no emission, TPT–perchlorate salt shows an emission both in solution and in the solid state. The emission and excitation spectra of TPT–TCP and TPT–perchlorate salts in the solid state at room temperature are given in Fig. 4. The emission of the perchlorate salt in the solid state is also found in fluid solution. This is assigned to the fluorescence of TPT cation by its lifetime in solution (a few ns), the mirror image relationship between the absorption and emission bands of the cation, and the excitation spectrum which approximately agrees with the absorption spectrum.

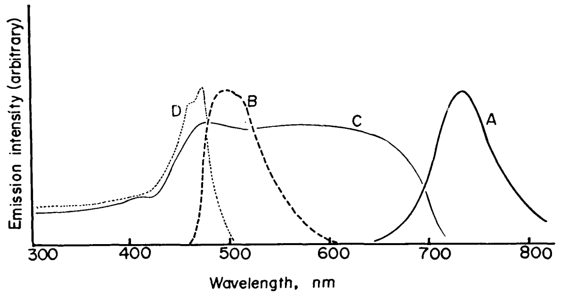

Fig. 4. Emission spectra of TPT-TCP and TPT-perchlorate salts in the crystalline state.
(A) emission spectrum of TPT-TCP, (B) emission spectrum of TPT-perchlorate, (C) excitation spectrum of the emission of TPT-TCP at 740 nm, (D) excitation spectrum of the emission of TPT-perchlorate at 500 nm.

In TPT–TCP in the solid state, the fluorescence of TPT cation was not found, and a new emission was observed at 740 nm which can be assigned to an interionic CT fluorescence for the following reasons: (i) the mirror image relationship with CT absorption holds, (ii) the emission can be found by irradiation not only in the LE band but also in the CT absorption band, (iii) the lifetime is much shorter than 100 μsec. The excitation spectrum of the emission (Fig. 4) does not coincide with the diffuse reflectance spectrum in Fig. 2b. This might be due to the insufficient transmission of the incident light into the microcrystalline sample.

The above assignment is confirmed by the fact that such an emission band is also found in the solid state of other organic CT salts (Fig. 1). The maximum wavelengths of the CT absorption and CT fluorescence bands of these salts are given in Table 2. An approximately parallel relationship is found between the energies of the absorption and emission bands. Thus, when a CT interaction is present, the fluorescence of the component ion is completely quenched and a CT fluorescence is observed in the solid state.

Table 2. Maxima of the CT fluorescence (λ^{F}_{max}) and the CT absorption band (λ^{A}_{max}) in the solid state

Salts	λ^{F}_{max} (nm)	λ^{A}_{max} (nm)
TPP-TCP	725	565
TPT-TCP	740	540
ADPP-TCP	640	530 (S)
ADPT-TCP	710	560 (S)
TPP-TCM	680	530
TPT-TCM	620	520 (S)
ADPP-TCM	670	520 (S)

(S): shoulder

Emission Spectrum in Fluid Solution. The emission spectrum of TPT–TCP in fluid solution was measured at room temperature in various solvents in various concentrations. In all cases, the fluorescence of TPT cation was observed, but not CT fluorescence. The intensity of the fluorescence of the cation was very sensitive to the solvent polarity, becoming weak with the decrease of the solvent polarity (Fig. 5). This suggests that the fluorescence of the cation is emitted only from the free TPT cation present in solution, and that the amount of the free cation produced by the dissociation of the ion-pair becomes small in a less polar solvent. This is supported by the fact that the excitation spectrum of this emission agrees with the absorption of TPT cation.

Thus, in fluid solution TPT–TCP shows only the fluorescence of the free TPT cation and no emission from the undissociated ion-pair. This is in sharp contrast to the observation of the CT fluoerscence of

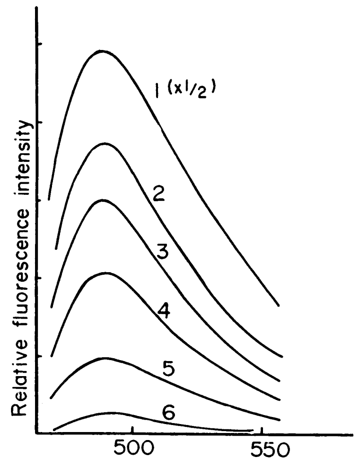

Fig. 5. Solvent effect of the emission spectrum of TPT-TCP salt in fluid solution at room temperature. (1) 2MTHF-C_2H_5OH (2 : 1), (2) 2MTHF, (3) 2MTHF-toluene (9.8 : 0.2), (4) 2MTHF-toluene (9.5 : 0.5), (5) 2MTHF-toluene (8 : 2), (6) 1,4-dioxane.

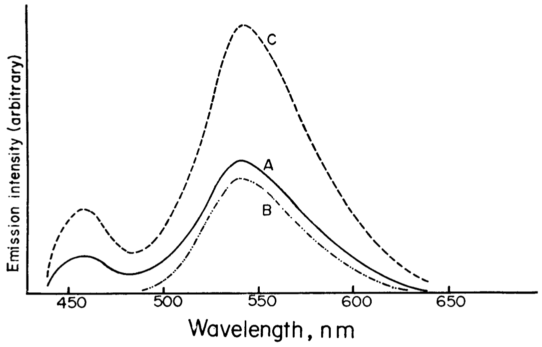

Fig. 6. Emission spectra of TPT-TCP and TPT-perchlorate salts in CH_3OH-C_2H_5OH (1 : 1) rigid solution at 77 K.
(A) total emission of TPT-TCP at 77 K, (B) delayed emission of TPT-TCP, (C) total emission of TPT-perchlorate.

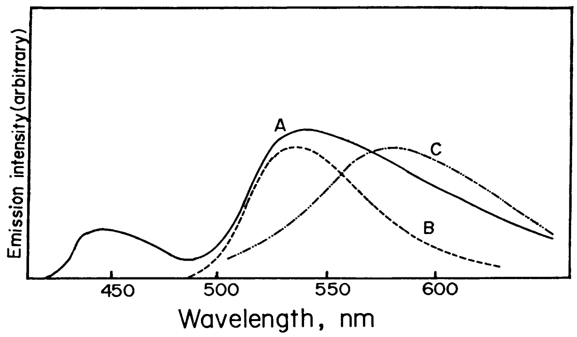

Fig. 7. Emission spectrum of TPT-TCP salt in 2MTHF-toluene (9 : 1) solution at 77 K.
(A) total emission by excitation at 420 nm, (B) delayed emission by excitation at 420 nm, (C) total emission by excitation at 470 nm.

TPT-TCP in the solid state. In fluid solution the CT excited energy can be deactivated without radiation because of the interionic CT interaction.[15] Similarly, an ordinary molecular CT complex does not show a CT fluorescence even in non-polar solvents except for a few rare cases. This could be understood in terms of an extremely low transition probability of a CT complex in fluid solution.[16—18]

It should be noted that with TPT–TCP the following case is also conceivable: A CT fluorescence emitted near the IR region could not be observed because of the limitation of the spectrofluorometer in the wavelength region longer than 800 nm. In *s*-tetracyanobenzene-polymethylbenzene complexes in which a CT fluorescence can be found in fluid solution, the Stokes shift of the CT transition at room temperature is 8000—12000 cm^{-1}, which is much larger than that in rigid solution at 77 K (4500—8300 cm^{-1}).[17,18] In TPT–TCP the Stokes shift in 2MTHF-toluene (9 : 1) rigid solution at 77 K is estimated to be 4200 cm^{-1}. If the Stokes shift at room temperature were greater than 6000 cm^{-1} as in tetracyanobenzene complexes, the CT fluorescence would have its maximum above 800 nm, which could not be detected by our apparatus.

Emission Spectrum in Rigid Solution at 77 K. The emission spectrum of TPT–TCP in rigid solution is also affected by the nature of the solvent. In a polar solvent, methanol–ethanol(1 : 1), it is essentially the same as that of TPT–perchlorate under the same conditions (Fig. 6). The emission band at 460 nm is the fluorescence of the cation. An emission band at 540 nm is assigned to the phosphorescence of TPT cation, since it is found as a delayed emission of the perchlorate salt at 77 K, its lifetime being about 30 ms. Since in this solvent TPT–TCP dissociates completely into two component ions, the two emissions originate from the free TPT cation present in rigid solution.

The emission spectra of TPT–TCP in a less polar 2MTHF–toluene (9 : 1) solution are shown in Fig. 7. In the case of the excitation of the LE band of the cation, the emission band at 540 nm becomes broad with a new emission around 600 nm. On the excitation of the CT band in rigid solution (at 470 nm), only the new emission was observed at 585 nm. The band can be assigned to the interionic CT fluorescence of TPT–TCP for the following reasons; (i) the lifetime is about 170 ns, (ii) a mirror image relationship holds between this emission band and the CT absorption band shown in Fig. 3, (iii) the Stokes shift of this transition, about 4200 cm^{-1}, is comparable with that of ordinary molecular CT complexes in rigid solution.[19]

The relative intensities of the three emission bands, the fluorescence and phosphorescence of the cation and the CT fluorescence, are very sensitive to solvent polarity. The total emission spectra of TPT–TCP by 420 nm excitation are shown in Fig. 8 for various compositions of 2MTHF–toluene solvent system. In a more polar solvent the phosphorescence of the cation is predominant over the CT fluorescence, while in a less polar solvent the CT fluorescence predominates. The relative intensity of the phosphorescence of the cation is plotted against the solvent composition in Fig. 9. The intensity of the phosphorescence is reduced strikingly with the addition of toluene, its lifetime remaining almost unchanged. Upon direct excitation of the CT absorption band, no phosphores-

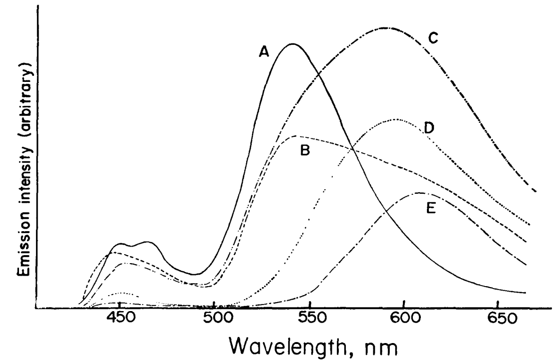

Fig. 8. Emission spectra of TPT-TCP salt in various compositions of 2MTHF-toluene solvent system at 77 K by excitation at 420 nm.
(A) 2MTHF, (B) 2MTHF-toluene (9 : 1), (C) 2MTHF-toluene (8 : 2), (D) 2MTHF-toluene (6.5 : 3.5), (E) 2MTHF-toluene (2 : 8).

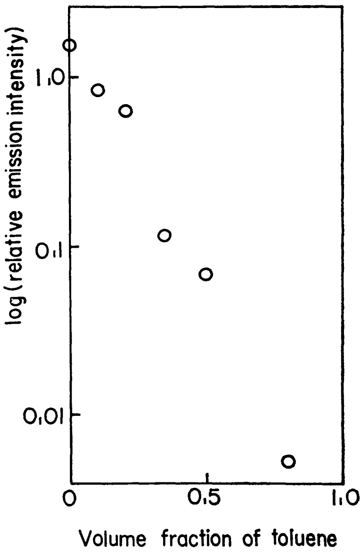

Fig. 9. Relative phosphorescence intensity of TPT cation against the solvent composition of 2MTHF-toluene.

cence of the cation be can observed. This indicates that even in a non-polar solvent the phosphorescence of the cation is emitted only from the dissociated free cation. Thus the dependence of the emission spectrum on the solvent polarity shown in Fig. 8 can be accounted for by the variation of the relative amount of the free TPT cation due to dissociation. This shows that the solvent polarity similar to that of 2MTHF–toluene (9 : 1) is required for the dissociation of the salt in rigid solution. This appears to correspond to the fact that in solution at room temperature the salt dissociates almost completely into two component ions in the solvent with $D>10$.

In the case of some molecular CT complexes, phosphorescence emission often occurs from the lowest CT triplet state which is generated by the intersystem-crossing *via* the CT singlet excited state. CT phosphorescence in particular which is similar to that of the component molecule, is observed in some complexes such as *s*-tetracyanobenzene–naphthalene complex.[20] In TPT–TCP, however, this is not possible since the energy of the phosphorescence is much higher than that of the CT fluorescence.

The solvent polarity is a very important factor in determining the emission spectrum of the interionic CT salt, the degree of dissociation of the salt being primarily determined by this factor. The solvent polarity also has an effect on the maximum wavelength and the lifetime of the CT fluorescence. The maximum wavelengths and lifetimes of the CT fluorescence, and the maximum wavelengths of the CT absorption in various solvents are listed in Table 3. Accurate determination of the maximum of the CT fluorescence is difficult with the excitation in the LE bands, since both the CT fluorescence and the phosphorescence of the cation are observed simultaneously. Thus, the maximum wavelengths given in Table 3 were determined by the excitation of the CT absorption band. The fluorescence lifetimes, however, were measured on the excitation at 337 nm of an N_2 gas laser.

TABLE 3. MAXIMUM WAVELENGTH (λ^F_{max}) AND LIFETIME (τ_F) OF CT FLUORESCENCE AT 77 K AND MAXIMUM WAVELENGTH (λ^A_{max}) OF THE CT ABSORPTION BAND IN VARIOUS SOLVENTS

Solvent	λ^F_{max} a) (nm)	τ_F b) (ns)	λ^A_{max} at 70 K (nm)	λ^A_{max} at 293 K (nm)
2MTHF	585	150	460(S)c)	585
2MTHF-toluene (9 : 1)	585	170	470	590
2MTHF-toluene (8 : 2)	590	240	—	595
2MTHF-toluene (6.5 : 3.5)	596	290	—	603
2MTHF-toluene (5 : 5)	600	—	—	625
2MTHF-toluene (2 : 8)	610	330	—	635
1,4-Dioxaned)	635	—	—	635

a) By CT absorption band excitation at 470 nm at 77 K. b) By N_2 gas laser excitation at 337 nm at 77 K. c) Shoulder. d) In a cloudy solid at 77 K.

The increase of solvent polarity causes a blue shift of the CT fluorescence. Its amount is comparable with that of the CT absorption maximum resulting from the increase of the solvent polarity in solution at room temperature. A CT fluorescence of organic CT salts in rigid solution has been reported by Brinen *et al.* on some alkylpyridinium–halide salts.[12] They observed the CT fluorescence of the salts in three solvents, *i.e.*, water, methanol–ethanol (1 : 4), and dichloromethane, and found no solvent effect on the energy of the CT fluorescence. Thus, our result is quite different from that for alkylpyridinium salts.

As a CT salt has an ionic ground state, an ion-pair is strongly solvated in the ground state. Even in Franck-Condon state, the salt is still strongly solvated, despite the fact that the components of the salt are neutral in the excited state. Brinen *et al.* suggested that the solvent-solute reorientation occurs during the relaxation of the excited state from the Franck-Condon state to a fluorescent CT state even in rigid solution. However, Kobayashi *et al.* have shown that in *s*-tetracyanobenzene complexes this kind of reorientation does not occur sufficiently during the relaxation in rigid solution at 77 K.[18] Our present observation of the blue shift of the CT fluorescence also suggests that the reorientation of the solvent molecules is insufficient at 77 K, and that the salt in the CT fluorescent state is still solvated in a similar fashion to that in the ground state. If the CT fluorescence of this salt could be observed in fluid solution, the energy would remain constant independent of the solvent polarity, since the reorientation of the solvent molecules would occur sufficiently in fluid solution.

The lifetime of the CT fluorescence becomes long with the decrease of solvent polarity. The increase of lifetime may be caused by the decrease of the radiative transition probability or the decrease of the radiationless transition probability of the excited ion-pair. If the emission probability decreases, the quantum efficiency of the CT fluorescence would show a considerable decrease corresponding to the increase of the fluorescence lifetime. Although the quantum efficiency of the CT fluorescence cannot be determined, since the concentration of the undissociating ion-pair in rigid solution is unknown, such a decrease of intensity of the CT fluorescence was not observed. This suggests that the dependence of the fluorescence lifetime is attributable to the decrease of the radiationless transition probability of the excited ion-pair in a less polar solvent.

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