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メタデータ	<p>言語: English</p> <p>出版者: Wiley</p> <p>公開日: 2020-01-22</p> <p>キーワード (Ja):</p> <p>キーワード (En): Solvatochromism, Solvent effects, Quinodimethanes, Electron acceptor, Molecular electronics</p> <p>作成者: 玉谷, 穂菜美, 鳥井, 悠人, 石川, 拓, 中野, 英之, 飯森, 俊文</p> <p>メールアドレス:</p> <p>所属:</p>
URL	http://hdl.handle.net/10258/00010102

Photophysics and Inverted Solvatochromism of 7,7,8,8-Tetracyanoquinodimethane (TCNQ)

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Abstract

We report the absorption, fluorescence, and Raman spectroscopy of 7,7,8,8-tetracyanoquinodimethane (TCNQ) in a variety of solvents. The fluorescence quantum yields (QYs) of linear alkane solutions are similar to one another, but QY is shown to acutely decrease in other solvents with increasing polarities. The slope of the solvatochromic plot of absorption maxima is inverted from negative to positive with an increase in solvent polarity. A significant change in the frequency of carbon-carbon double bond stretching modes is not observed in Raman spectra of TCNQ in different solvents. The molar absorption coefficient is determined to calculate the oscillator strength of the absorption band. The radiative decay rate constant calculated from the oscillator strength is approximately ten times larger than that elucidated from the fluorescence lifetime and QY. These spectroscopic parameters reveal that the relaxation occurs from a Franck-Condon excited state to a distinct fluorescence emissive state with a smaller transition dipole moment.

Keywords

Solvatochromism; Solvent effects; Quinodimethanes; Electron acceptor; Molecular electronics

Introduction

7,7,8,8-tetracyanoquinodimethane (TCNQ) (Fig. 1) is a versatile electron acceptor molecule that is used as a building block for a number of functional materials and molecular assemblies.^[1-15] TCNQ has been an important molecule in solid-state chemistry for the synthesis of charge-transfer (CT) complexes with high electrical conductivity.^[1,2,6,8] In direct relation to the properties of CT complexes, there are a number of studies on the electronic states and the structure of the radical anion $\text{TCNQ}^{\bullet-}$ by using quantum chemical calculations, vibrational spectroscopy, absorption spectroscopy, and electron spectroscopy.^[16-26] In comparison to the radical anion, the understanding of the electronic state and the photophysics of the neutral TCNQ is still very limited. Absorption spectra in the gas phase and in a variety of media were reported by Pennelly et al.^[27] Vibrational normal modes of TCNQ and deuterated TCNQ were studied in the crystal phase with infrared (IR) and Raman spectroscopy.^[28,29] A previous study of the photoluminescence of TCNQ in 2-methyl-tetrahydrofuran at 77 K showed that the fluorescence of both TCNQ and $\text{TCNQ}^{\bullet-}$ was rather weak.^[30] The excited state dynamics in the first excited singlet (S_1) state in acetonitrile were investigated by using transient absorption spectroscopy.^[31] Ultrafast relaxation of the S_1 state was observed, leading to very weak fluorescence in acetonitrile. The main deactivation process was assigned to the efficient internal conversion to the ground state.^[31] A fluorescence spectrum with a fluorescence maximum at 459 nm was also reported for carbon tetrachloride.^[32] Energy levels of several electronically excited states of TCNQ were calculated with a density functional theory (DFT) calculation, and the oscillator strength of the S_1 - S_0 transition was reported to be $f = 1.07$.^[33] Weak photoluminescence of some derivatives of TCNQ was also reported.^[34]

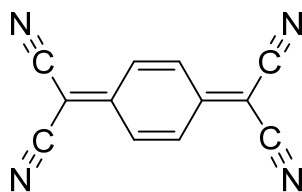


Figure 1. Chemical structure of TCNQ.

We have recently investigated the photophysics of neutral TCNQ by solvatochromism and photoluminescence studies in a few solvents. We reported that neutral TCNQ emits blue fluorescence with a quantum yield (QY) of ca. 0.1 in hexane.^[35] In addition, using six different solvents, we concluded that the fluorescence of TCNQ showed an acute response to subtle changes in the polarity of the solvent. Laser-induced fluorescence (LIF) spectroscopy in a cold gas phase was also reported recently to gain insight into the structure and the electronic excited state of neutral TCNQ.^[36] The position of the 0-0 band of the S_1 - S_0 electronic transition was determined to be 412.13 nm (24262 cm^{-1}) in the gas phase. The fluorescence lifetime of the S_1 state at the zero-point level was 220 ns. This lifetime was surprisingly longer than the fluorescence lifetime in hexane, 4.5 ns,^[35] indicating that the fluorescence lifetime becomes shorter by more than 40 times even in a nonpolar solvent in comparison to that observed in the gas phase. At present, the understanding of the mechanism behind these observations is far from satisfactory. An evaluation of the oscillator strength in hexane is of fundamental importance to discuss the large gap in the fluorescence lifetimes between that observed in the gas phase and that seen in solution. However, it has not been reported, to the best of our knowledge. Spectroscopic characterization by using more solvents than the previous work is also useful as supporting evidence of the unusual photophysics of TCNQ.

Here, we report a detailed account of the comprehensive spectroscopic characterization of TCNQ in a variety of solvents to gain understanding of the photophysics of TCNQ. An inversion phenomenon of solvatochromism of the absorption band is reported. The solvation structure is studied in terms of a solvatochromic plot obtained using a mixture of solvents. The molecular structure of TCNQ in the ground state is probed by Raman spectroscopy for carbon-carbon stretching modes. The radiative decay rate constant is estimated from spectroscopic parameters such as the molar absorption coefficient, the fluorescence QY, and the fluorescence lifetime. The characteristics of the electronic states that are related to the fluorescence of TCNQ are argued.

Results and discussion

Solvatochromism and relative fluorescence quantum yield

Absorption, fluorescence, and fluorescence excitation spectra in nonpolar 2-methylbutane, *n*-pentane, *n*-heptane, *n*-octane, and 2,2,4-trimethylpentane are shown in Fig. 2. The results for *n*-hexane and cyclohexane have been reported elsewhere.^[35] The absorption maximum is summarized in Table 1. The polarity is scaled by the Onsager polarity function, which is defined by $f(D) = 2(D - 1)/(2D + 1)$, where D is the dielectric constant.^[37] The absorption maximum for 2-methylbutane is observed at the shortest wavelength of 389 nm, shifting to a longer wavelength with the increase in $f(D)$ for the other solvents. The absorption maximum for 2,2,4-trimethylpentane slightly deviates from this trend. The absorption band is assigned to the neutral monomer of TCNQ.^[27,35,36] Fluorescence excitation spectra for all solvents match the corresponding absorption spectra. Therefore, the fluorescence bands can also be assigned

to the neutral TCNQ monomer. Impurities including the radical anion $\text{TCNQ}^{\bullet-}$ and reaction products of TCNQ with impurities in the solvents made no contribution to the spectra.

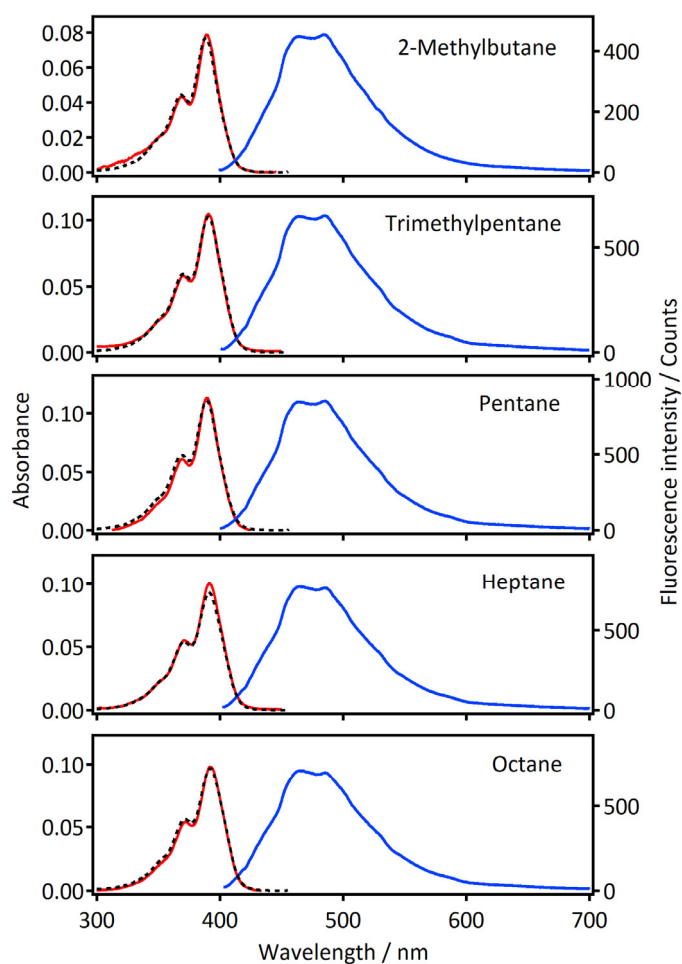


Figure 2. Absorption spectra (red), fluorescence spectra (blue) excited at the absorbance maxima of TCNQ, and the fluorescence excitation spectra (broken line). The fluorescence excitation spectra were measured by detecting the fluorescence at 465 nm for trimethylpentane and at 466 nm for the other solvents.

Table 1. Absorption maxima (λ_{abs}) and fluorescence maxima (λ_{fl}) of TCNQ in different solvents.

Number ^a	Solvents	$f(D)^b$	$\lambda_{\text{abs}} / \text{nm}$	$\lambda_{\text{fl}} / \text{nm}$
1	2-Methylbutane	0.36	389	465 and 485
2	<i>n</i> -Pentane	0.36	390	464 and 485
3	<i>n</i> -Hexane	0.37	391 ^c	465 and 485
4	<i>n</i> -Heptane	0.38	392	465 and 486
5	<i>n</i> -Octane	0.39	393	465 and 486
6	2,2,4-Trimethylpentane	0.39	391	464 and 485
7	Cyclohexane	0.41	394 ^c	468 and 486
8	Decaline	0.44	399	467
9	Carbon tetrachloride	0.45	397 ^c	468
10	Tetrachloroethylene	0.46	401	503
11	Trichloroethylene	0.62	403	523
12	Chloroform	0.72	401 ^c	473
13	Dichloromethane	0.84	401 ^c	471
14	1,2-Dichloroethane	0.86	402	480
15	Acetone	0.93	396	485
16	Acetonitrile	0.96	393 ^c	481

^aNumbers used in Figs. 4 and 7.

^bThe Onsager polarity function of the solvents.^[37] $f(D) = 2(D - 1)/(2D + 1)$, where D is the dielectric constant of the solvent.^[38-40]

^cRef. [35].

Absorption and fluorescence spectra for the more polar solvents are shown in Fig. 3. TCNQ \bullet^- was formed quickly in acetone, and thus we had to prepare the acetone solution without Ar gas bubbling to quickly make measurements after the preparation of the solution. The solvatochromic plot of the absorption maxima is shown in Fig. 4. The data for some of the solvents reported elsewhere^[35] are reproduced in Fig. 4. The absorption maximum was redshifted with the increase in $f(D)$ in the range of $f(D) < 0.6$. For the solvents with $f(D)$ values between 0.6 and ~ 0.9 , the absorption maxima were nearly constant. The absorption maxima in acetone and acetonitrile showed a steep blueshift from $24.8 \times 10^3 \text{ cm}^{-1}$ observed in dichloroethane to $25.4 \times 10^3 \text{ cm}^{-1}$ observed in acetonitrile.

The steep blueshift of the absorption maximum for $f(D)$ in the range from 0.84 for dichloromethane to 0.96 for acetonitrile was examined by using mixtures of the two solvents. Liquid mixtures with different compositions were prepared and handled in air. The absorption spectra taken by using the mixtures of acetonitrile and dichloromethane are shown in Fig. 5a. The shift of the absorption maximum was observed with the change in the volume fraction of acetonitrile (x_{AN}). The solvatochromic plot as a function of x_{AN} is shown in Fig. 5b. We observed a nearly linear relationship between the absorption maximum and x_{AN} . When there is a specific interaction such as hydrogen bonding or the preferential solvation of solvent, the solvatochromic plot, in general, shows a deviation from linearity.^[37] The linearity of the solvatochromic plot in Fig. 5b indicates that the solvatochromic shift is induced by a change in the intrinsic polarity of the mixture. A similar result was observed for mixtures of dichloromethane and hexane.^[35]

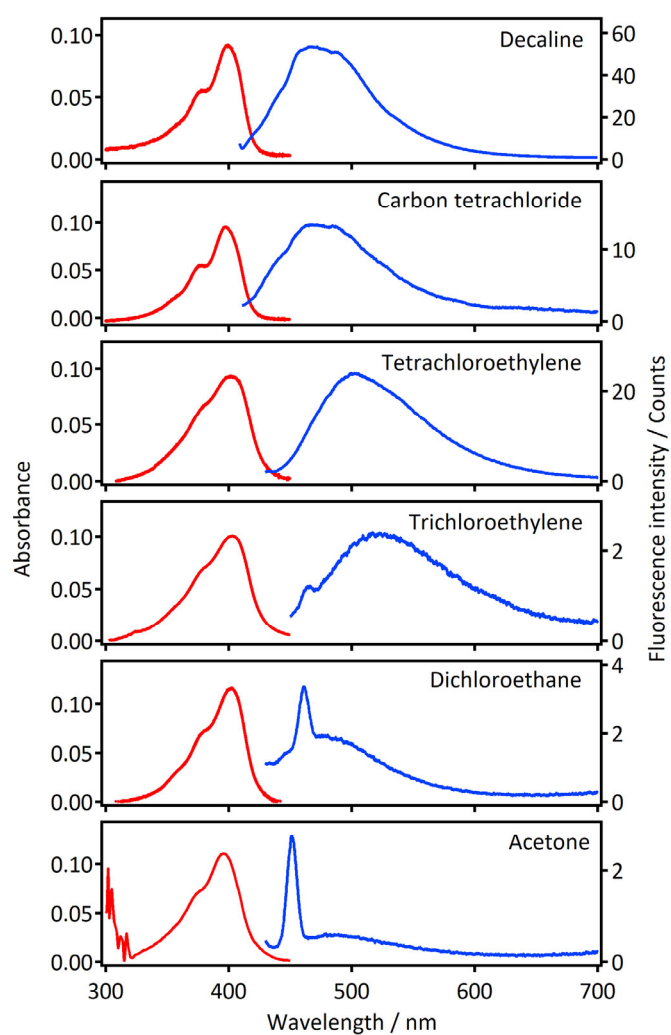


Figure 3. Absorption spectra (red) and fluorescence spectra (blue) excited at the absorbance maxima of TCNQ. The sharp bands that appear in the range from 450 to 470 nm in the fluorescence spectra are the Raman scattering bands of the solvents.

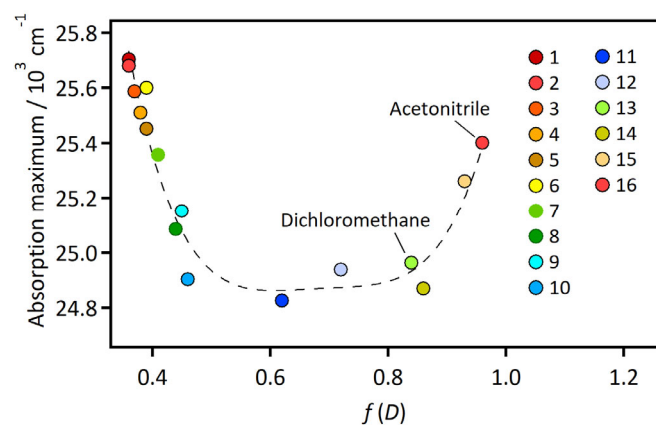


Figure 4. Solvatochromic plot of the absorption maximum versus the polarity function of solvents: 1, methylbutane; 2, *n*-pentane; 3, *n*-hexane; 4, *n*-heptane; 5, *n*-octane; 6, 2,2,4-trimethylpentane; 7, cyclohexane; 8, decaline; 9, carbon tetrachloride; 10, tetrachloroethylene; 11, trichloroethylene; 12, chloroform; 13, dichloromethane; 14, dichloroethane; 15, acetone; 16, acetonitrile. The dashed line provides trend visualization.

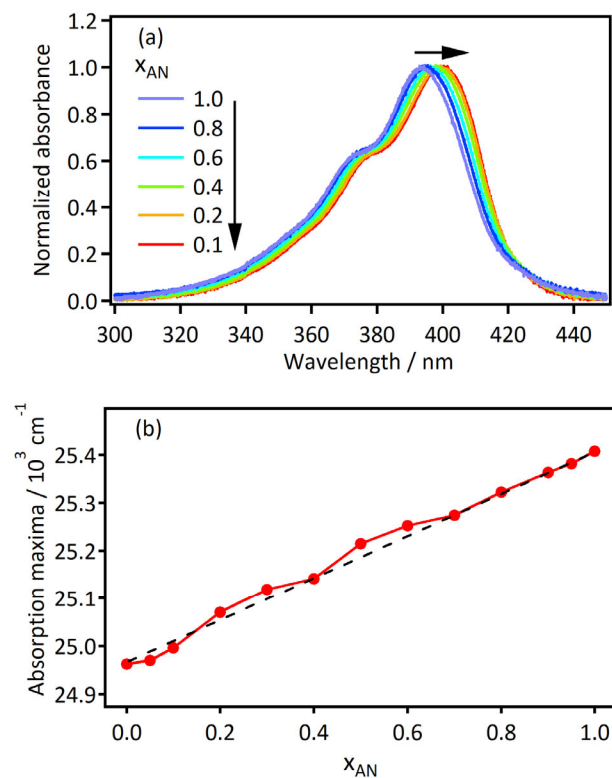


Figure 5. (a) Normalized absorption spectra for the mixture of acetonitrile and dichloromethane. x_{AN} is the volume fraction of acetonitrile. (b) The absorption maximum as a function of x_{AN} in the mixture. A dashed line connects the two ends of $x_{AN} = 0$ and $x_{AN} = 1$.

The solvatochromic plot as a function of $f(D)$ was not linear but rather concave (Fig. 4). The shift was inverted from a bathochromic (red) shift to a hypsochromic (blue) shift with an increase in $f(D)$. The absorption maximum of molecules that have no specific interaction or preferential solvation, in general, shows a linear dependence on the polarity of solvents. Exemplary molecules that exhibit similar inversion of the solvatochromism are merocyanine dye molecules.^[38,41,42] The inversion of the solvatochromism for merocyanine dyes was explained by the alternation of the ground state structure between the quinoid structure and the benzenoid structure in solvents with different polarities. The modification of the molecular structure between the two resonance structures was experimentally verified through the measurement of dipole moments for the ground state and the Franck-Condon (FC) excited state using Stark spectroscopy.^[42] The electronic state of TCNQ can also be represented by a hybrid of the quinoid structure and the benzenoid structure, as shown in Fig. 6. When the molecular structure is altered between these two structures, a change in the frequency of the stretching mode of the carbon-carbon double bond is expected. Therefore, the contribution of each resonance form in the ground state can be investigated by Raman spectroscopy. The results of Raman spectroscopy and discussion on the mechanism of the inverted solvatochromism will be described in the following section.

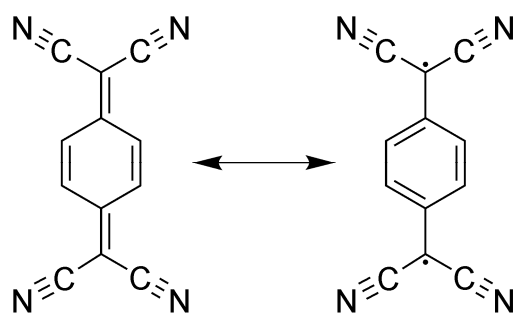


Figure 6. Quinoid (left) and benzenoid (right) structures of TCNQ.

The fluorescence QY of TCNQ in *n*-hexane has been reported as 0.11.^[35] As demonstrated in Figs. 2 and 3, the fluorescence intensity was sensitive to the polarity of the solvent. The absorbance of each of the solutions used in this work was adjusted to approximately 0.1. The deviation from linearity in the relation between fluorescence intensity and absorbance is known as the inner filter effect.^[43,44] It is generally recommended that the absorbance should be kept below 0.05 to render the inner filter effect negligible. Although the apparent fluorescence QY at the absorbance of 0.1 used in this work will be only ~10 % smaller than that observed for an infinitely dilute solution,^[43,44] the absorbance is slightly higher than the recommended condition. However, the inner filter effect can be regarded as approximately identical for all of the solutions. Therefore, we can take the fluorescence intensity divided by the absorbance as a relative measure of the fluorescence QY among the solutions. The relative fluorescence QY as a function of $f(D)$ is shown in Fig. 7. The fluorescence QY for *n*-pentane, *n*-hexane, *n*-heptane, and *n*-octane are very similar to each other. When the $f(D)$ was increased to that for cyclohexane ($f(D) = 0.41$), the fluorescence QY was decreased to ca. 60% of that for hexane. In decaline and carbon tetrachloride, the fluorescence QY was smaller than 10% of that for hexane, that is, smaller than 0.01. The fluorescence QY for solvents having higher $f(D)$ values than trichloroethylene was estimated to be smaller than 0.001. The fluorescence QY of TCNQ acutely decreased with increasing solvent polarity.

The fluorescence spectra showed two maxima (Fig. 2), which are probably ascribed to the progression of the ground state^[36] in the nonpolar solvents having $f(D)$ values lower than that of decaline (Table 1). For the more polar solvents, the fluorescence band became broad, so the estimation of the position of the fluorescence maximum contained errors. Overall, the fluorescence maximum apparently showed a redshift with increasing $f(D)$ of the solvent. An exceptionally large redshift was observed for tetrachloroethylene and trichloroethylene. These molecules have a carbon-carbon double bond, which is an electron-rich functional group. We

speculate that charge-transfer complexes of TCNQ with these solvent molecules are formed in the excited state to emit exciplex fluorescence.

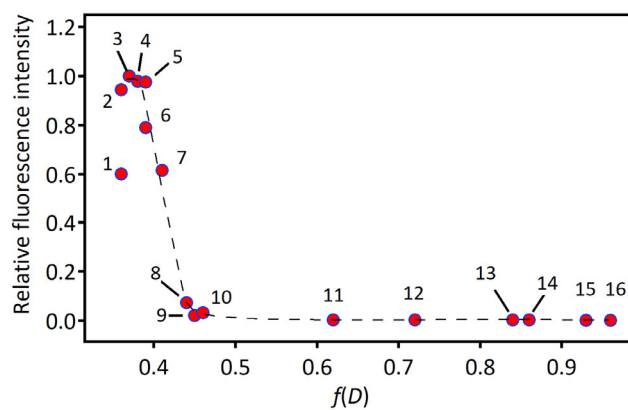


Figure 7. Relative fluorescence quantum yield in comparison with hexane as a function of $f(D)$. The dashed line provides trend visualization. See Table 1 and Fig. 4 for the solvent codes.

Raman spectra of TCNQ in different solvents

We examined the contribution of the resonance structure of TCNQ in the ground state in different solvents using Raman spectroscopy. Raman spectra of the neutral TCNQ have been reported in solution in acetonitrile^[21] and in crystalline form.^[28,29] Strongly observed normal modes are composed of symmetric C≡N stretching, ring carbon-carbon single bond (C–C) stretching, ring carbon-carbon double bond (C=C) stretching, C–H bending, and wing C=C stretching.^[28] It is known that the frequencies of the C=C stretching modes reflect the π -bond order in TCNQ.^[21,32] When the contribution of the benzenoid resonance form becomes greater (Fig. 6), the frequency of the wing C=C stretching mode is expected to decrease due to the greater contribution of the C–C bond character. Accordingly, the shift of the frequency of the wing C=C stretching mode is expected, as the contribution of the quinoid resonance form is changed with the polarity of the solvent.

Raman spectra are presented in Fig. 8, and the observed frequencies are summarized in Table 2. The excitation wavelength of 325 nm was close to the absorption maximum, and thus, the spectra in Fig. 8 were actually regarded as resonance Raman scattering. A strong background signal was detected for hexane, probably due to degraded products of TCNQ or accidental contamination from unknown fluorescent materials. We could detect the Raman bands of TCNQ superimposed on the background signal. For cyclohexane and acetonitrile, the negative signals clearly appear at 1270 and 2250 cm^{-1} , respectively, in the Raman spectra of TCNQ. These signals are artifacts due to incomplete subtraction of the Raman bands derived from the solvents. The artifacts were unavoidable because of the stronger intensity of the Raman bands derived from the solvents in comparison to the signal of TCNQ. The observed frequencies in the crystal are also shown in Table 2. In crystalline form, TCNQ has a quinoid structure.^[45] The frequencies for acetonitrile were in good agreement with the

previously reported results using the same solvent.^[21] The ν_2 mode is the symmetric C \equiv N stretching mode,^[28] hardly changing the frequency in the different solvents. The normal coordinates for the ν_3 and ν_4 modes are depicted in Fig. 9.^[36] The ν_3 mode has a large contribution from ring C=C stretching. The ν_4 mode is mainly wing C=C stretching. The ν_5 mode is composed of C–H bending and ring C=C stretching. There was no significant change in the frequencies of the ν_3 and ν_5 modes when the solvent was changed. Although the ν_4 mode possibly shows a +10 cm⁻¹ shift upon increasing $f(D)$ from cyclohexane to acetonitrile, the magnitude of the shift is too insignificant to conclude that there is a change in the contribution of the resonance structure with the increase in $f(D)$. The good agreement of the frequencies of the carbon-carbon bond stretching modes for the crystal and the solvents implies that the contribution of the resonance structure is similar both in the crystal and in the solvents. In summary, using Raman spectroscopy, we could not find clear evidence that the inversion of the solvatochromism was caused by the alternation of the electronic structure between the quinoid and benzenoid resonance forms.

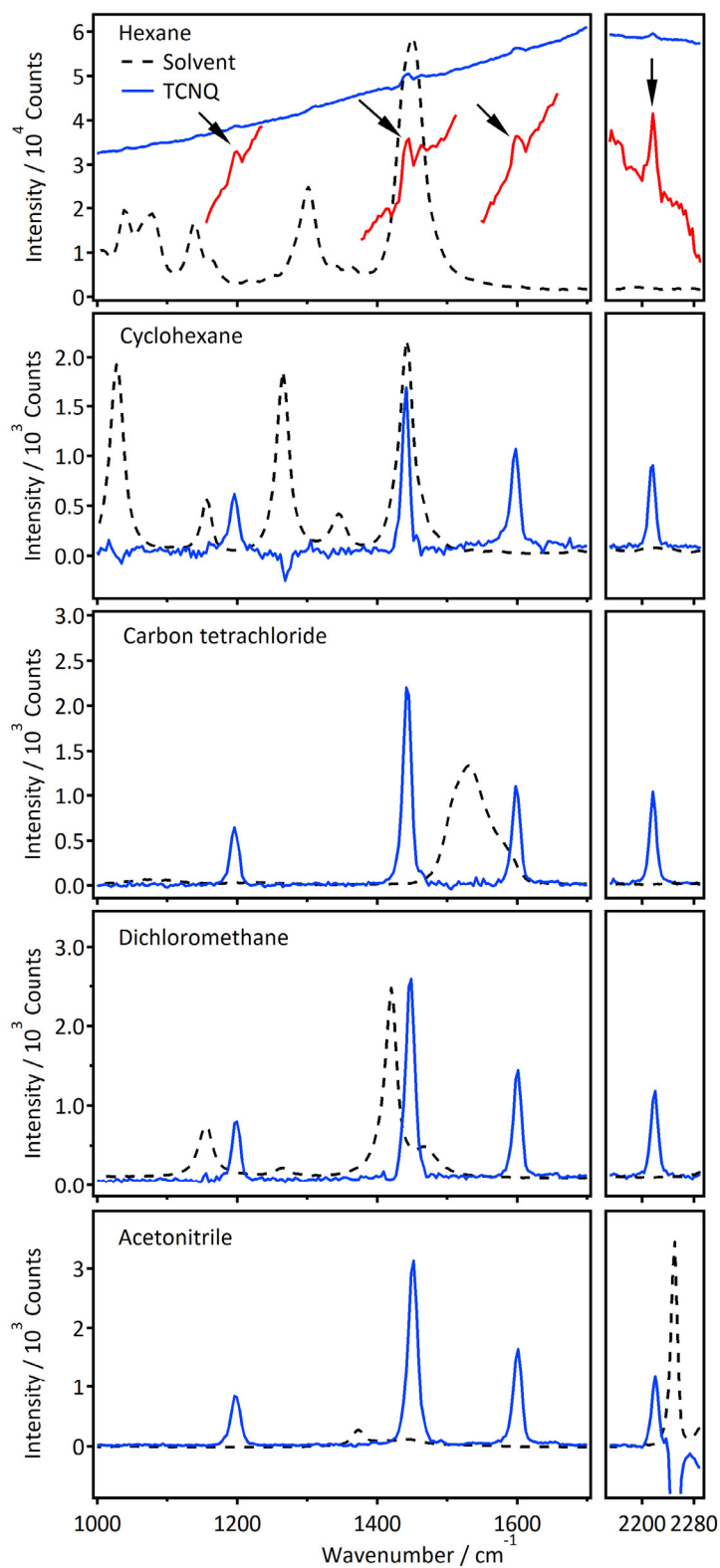


Figure 8. Raman spectra of TCNQ (blue) and the solvents (dashed line). A strong background signal is detected in the Raman spectrum in hexane. The scale of the intensity for

hexane is enlarged, and the spectra are depicted after offsetting using the red line. The arrows on the enlarged spectra indicate the Raman bands derived from TCNQ. The strong Raman signal arising from the solvents is responsible for the negative features observed in cyclohexane and acetonitrile.

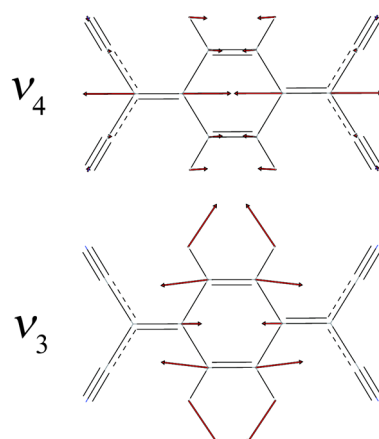


Figure 9. The normal coordinates for the ν_4 and ν_3 modes of the ground state of TCNQ originally published in Ref. 36 and reproduced with permission.

Table 2. Normal modes and frequencies (cm^{-1}) observed in the Raman spectra of TCNQ.

Mode ^{a, b}	Hexane	Cyclohexane	Carbon tetrachloride	Dichloro- methane	Acetonitrile	Crystal ^a	Acetonitrile ^c
ν_2	2217	2217	2217	2220	2220	2225	2223
ν_3	1598	1598	1598	1602	1602	1600	1603
ν_4	1445	1442	1442	1449	1452	1454	1453
ν_5	1196	1196	1196	1196	1196	1206	1198

^a Ref. [28].

^b Ref. [36].

^c Ref. [21].

The mechanism of the inversion of the solvatochromism is not clear at present. One possible explanation is that different electronic states with different charge distributions might be nearly degenerated to make the absorption band, which seemingly originates from a single electronic state. In this case, the absorption band is actually composed of two overlapping absorption bands. If the two absorption bands show distinct solvatochromic shifts and the absorption coefficients for the two bands change with $f(D)$, the inversion of the absorption maximum might seemingly appear. However, the calculation of the excited states using the time-dependent (TD) DFT method has predicted that there is only a single excited state near the observed absorption band.^[33] On the grounds of this DFT calculation, the contribution of nearly degenerated electronic states should be rejected. Another possible explanation is that the change in the FC factor is induced by the change in the potential energy surface of the excited state. The presence of coupling with either the triplet state or the intramolecular charge-transfer (ICT) state in the excited state has been discussed in previous studies.^[35,36] Khvostenko et al. reported that the T_1 state is lower than the S_1 state by 1.18 eV.^[33] The T_1 or higher T_n triplet states can couple with the S_1 state. The energy gap between the FC excited state and the coupled state can change in different solvents. This change might also lead to a change in the excited-state potential energy surface, resulting in the modification of the FC factor. For an unambiguous explanation of the solvatochromism of TCNQ, we must await future studies about the structure and energy levels of the excited states.

Molar absorption coefficient in hexane

The observed fluorescence lifetime for the zero-point level of the S_1 state was 220 ns in the gas phase.^[36] This lifetime was much longer than the natural lifetime, which was predicted by

the quantum chemical calculation of the oscillator strength.^[33] It is useful to experimentally determine the molar absorption coefficient ε for the understanding of the photophysics of TCNQ under environments in which fluorescence is observed. Although the determination of ε in the gas phase is not straightforward, we can determine ε in a nonpolar solvent in which TCNQ emits fluorescence. The solubility of TCNQ is not good in nonpolar solvents such as hexane and cyclohexane. In fact, more than 100 mL of hexane was necessary to completely dissolve only 1 mg of TCNQ at room temperature. Moreover, the accurate measurement of a mass less than 1 mg was difficult when a conventional electronic balance was used. It is necessary to use a very large volumetric flask and an excessive amount of solvent if we prepare the solution with satisfactory accuracy. To circumvent these practical limitations, we first dissolved 10 mg of TCNQ in 250 mL of dichloromethane to obtain a solution with a concentration of 2.0×10^{-4} M. An amount of the prepared solution (0.5 mL) was then transferred to a volumetric flask and diluted to 100 mL by using pure hexane. The volume fraction of dichloromethane (x_{DCM}) in the solution obtained was 0.5%. We prepared the solution in air. We obtained $\varepsilon = 7.4 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ at 391 nm by using this solution. This value is close to the reported values of $\varepsilon = 6.36 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ at 395 nm in acetonitrile,^[3] $\varepsilon = 7.2 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ in chloroform,^[27] and $\varepsilon = 8.7 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ in 1,2-dibromoethane.^[33] Although the solution was actually a mixture of hexane and dichloromethane, x_{DCM} was very small. Absorption spectra for mixtures of hexane and dichloromethane have been reported elsewhere.^[35] The difference in the absorption bands between the mixture with $x_{\text{DCM}} = 0.005$ (0.5 %) and pure hexane ($x_{\text{DCM}} = 0$) was negligibly small. Thus, we can regard the molar absorption coefficient obtained in this work as what would be obtained when TCNQ was dissolved in pure hexane.

Spectroscopic parameters in hexane

The oscillator strength f can be related to the integration of the absorption band,^[46]

$$f = 4.3 \times 10^9 \int \varepsilon(\bar{\nu}) d\bar{\nu} , \quad (1)$$

where $\bar{\nu}$ is the wavenumber in the unit of cm^{-1} . Using the absorption spectrum in hexane,^[35] we obtained $f = 0.84$. The radiative decay rate constant (Γ) in hexane can be calculated by using the following equation,^[43,47]

$$\Gamma = 2.88 \times 10^{-9} n^2 \frac{g_l}{g_u} \frac{\int I_{FL}(\bar{\nu}) d\bar{\nu}}{\int \bar{\nu}^{-3} I_{FL}(\bar{\nu}) d\bar{\nu}} \int \varepsilon(\bar{\nu}) d\ln\bar{\nu} \quad (2)$$

where n is the refractive index of the solvent, g_l and g_u are the multiplicities of the ground and the excited states, and $I_{FL}(\bar{\nu})$ is the fluorescence intensity at $\bar{\nu}$. Both g_l and g_u are equal to 1 in the present study because our concern is fluorescence. The fluorescence spectrum in pure hexane was used as $I_{FL}(\bar{\nu})$ in the calculation. The natural lifetime τ_0 is given by $1/\Gamma$. We obtained $\Gamma = 3.2 \times 10^8 \text{ s}^{-1}$ and $\tau_0 = 3.1 \text{ ns}$.

The observed fluorescence lifetime τ in hexane was 4.5 ns.^[35] The natural lifetime that was evaluated from ε is close to this value, suggesting that the fluorescence QY should be close to $\Phi_F = 1$. However, the observed fluorescence QY of TCNQ in hexane was only $\Phi_F = 0.11$.^[35] This result indicates that the radiative decay rate constant for fluorescence in hexane is reduced from that evaluated from the ε of the absorption band. In fact, the radiative decay rate constant calculated from the observed fluorescence properties in hexane was $\Gamma = 2 \times 10^7 \text{ s}^{-1}$.^[35] This value is nearly one tenth of that evaluated from the ε of the absorption spectrum. The difference in Γ indicates that the fluorescence is emitted from a distinct electronic state from the FC excited state.^[43]

The fluorescence intensity, in general, shows a significant dependence on solvent polarity when an ICT state forms following photoexcitation.^[43] Thus, the acute response of the fluorescence QY on the solvent polarity (Fig. 7) is explained by assuming that there are two

excited states of the locally excited (LE) state and ICT state. If the energy gap between a triplet state and the S_1 state changes in different solvents, the intersystem crossing (ISC) rate to the triplet state must also change. This difference in the ISC rate may also explain the observed fluorescence property.

The oscillator strength f of the absorption spectrum depends on the transition dipole moment between the FC excited state and the ground state. When the FC excited state is coupled to other electronic states that have smaller transition dipole moments, the f and the corresponding Γ for the fluorescence spectrum can become smaller than those for the absorption band. Moreover, the fluorescence lifetime for the coupled state becomes longer than that expected from the f of the absorption band. The value of f of the absorption spectrum in hexane is not very different from the value ($f = 1.07$) for the S_1 - S_0 transition, which was predicted by a TD-DFT calculation.^[33] The S_1 state was assigned to the $^1B_{3u}$ state,^[36] which corresponds to the FC excited state of TCNQ in hexane. In a gas-phase free jet, the fluorescence lifetime excited at the zero-point level of the S_1 state was unusually longer in comparison with the natural lifetime estimated from $f = 1.07$.^[36] In addition, a strong dependence on the vibronic bands was observed in the fluorescence lifetime. The fluorescence lifetime excited at the vibronic band of the ring deformation mode was longer than the zero-point of the S_1 state, reaching 300 ns.^[36] This result shows that the upper limit of the radiative decay rate constant in the gas phase is $\Gamma = 1/(300 \text{ ns}) = 3.3 \times 10^6 \text{ s}^{-1}$. This value is approximately one hundredth of the Γ evaluated from the oscillator strength of the absorption band. The unusually small Γ for the fluorescence in the gas phase and in the solvent can be explained by a coupling of the S_1 state with a nearby electronic state having a much smaller transition dipole moment. It is likely that the electronic state that couples with the S_1 state is either a triplet state or an ICT state.^[35,36] We conclude that the coupling between the FC excited state and a triplet state or an ICT state is a clue to understanding the fluorescence dynamics not only in the gas phase but also in solvents.

Conclusions

We obtained a new physical insight into the photophysics of TCNQ by extending our preliminary study. Although the fluorescence QY in linear alkanes was similar to one another, it showed a steep decrease in the range from $f(D) = 0.4$ to $f(D) = 0.45$. The slope in the solvatochromic plot of the absorption maxima versus $f(D)$ was inverted. A steep blueshift was observed between acetonitrile and dichloromethane. The preferential solvation was absent for the two solvents. The relationship between the inversion phenomenon of the solvatochromism and the molecular structure of the ground state was investigated using Raman spectroscopy. The frequencies of the carbon-carbon bond stretching modes and the $\text{C}\equiv\text{N}$ stretching mode were nearly identical for the polar and nonpolar solvents. It was therefore implied that the contribution of the resonance structure was almost independent of the polarity of the solvents. The molar absorption coefficient of the S_1 - S_0 absorption band was determined to calculate the oscillator strength. The radiative decay rate constant calculated from the molar absorption coefficient was approximately ten times larger than that evaluated from the fluorescence lifetime and QY. These spectroscopic parameters quantitatively demonstrated the importance of the coupling between the FC excited state and a different electronic state with a smaller transition dipole moment in the photophysics of TCNQ in solvent.

Experimental Section

TCNQ (Tokyo Chemical Industry) was recrystallised with acetonitrile and washed with benzene. 2-Methylbutane (Junsei Chemical, special grade), *n*-pentane (Junsei Chemical, special grade), *n*-heptane (Wako Pure Chemical Industries, spectrochemical analysis grade), *n*-

octane (Acros, extra pure grade), 2,2,4-trimethylpentane (Wako Pure Chemical Industries, spectrochemical analysis grade), tetrachloroethylene (Wako Pure Chemical Industries, special grade), trichloroethylene (Wako Pure Chemical Industries, special grade), 1,2-dichloroethane (Wako Pure Chemical Industries, spectrochemical analysis grade), and acetone (Wako Pure Chemical Industries, spectrochemical analysis grade) were used as received. Decaline (decahydronaphthalene) (Nacalai Tesque Inc., cis+trans, > 98%, GR grade) was washed with H₂SO₄ and aqueous sodium carbonate, dried with CaSO₄, and then distilled at reduced pressure. Prior to use in fluorescence measurements, the solutions were bubbled with Ar gas, handled in Ar gas-filled glove box, and contained in a stoppered quartz cell with an optical path length of 1 cm, unless otherwise noted. The concentration of TCNQ was ca. $2 \times 10^{-6} \text{ mol L}^{-1}$.

Raman spectra of the solutions of TCNQ were measured using a Raman microscope spectrometer (Renishaw, inVia). An output of 325 nm from a He-Cd laser (Kimmon Koha) was used as a light source with an attenuator. A stoppered quartz cell was used as a sample container. For acetonitrile, dichloromethane, and carbon tetrachloride, Raman spectra were measured at room temperature. For hexane and cyclohexane, the solubility of TCNQ at room temperature was too low to obtain a Raman scattering signal derived from TCNQ. The solutions of these solvents were heated in a flask to 60-70 °C by using a water bath to increase the solubility and were then transferred to the stoppered quartz cell. The solution in the cell was heated again just before the measurement of Raman spectra. The concentration of TCNQ for the Raman experiment was ca. $4 \times 10^{-5} \text{ mol L}^{-1}$. Raman spectra of TCNQ were obtained by subtracting the spectra of pure solvents from the spectra of the solutions of TCNQ.

Acknowledgements

Raman spectra were measured in Chitose Institute of Science and Technology under a support from Nanotechnology Platform Program (Synthesis of Molecules and Materials) of

the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan. This work was partly supported by JSPS KAKENHI Grant Number JP16K05950. TI acknowledges the CASIO science promotion foundation and the Suhara memorial foundation. We thank Dr. K. Kawano at Chitose Institute of Science and Technology for his assistance in the measurement of Raman spectra.

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