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Effect of Rigidity of Microenvironment on Fluorescence of 7,7,8,8- Tetracyanoquinodimethane (TCNQ)

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Abstract

We report the effect of rigidity of microenvironments on the fluorescence quantum yield (QY) of TCNQ dispersed in polymers which have different glass transition temperatures. The fluorescence QY decreases by increasing the temperature, which suggests that the nonradiative decay process is thermally activated. A pronounced decrease in the fluorescence QY is observed when the transition occurs from the glass state to the rubber state. The fluorescence QYs in solvents that have the similar polarity to PMMA and PVAc are smaller than those for these polymers. It is demonstrated that the nonradiative decay process is accompanied by structural deformation.

Keywords : Solvatochromism; Excited state dynamics; Solvent polarity; Fluorescence spectroscopy; Electron acceptor

1. Introduction

7,7,8,8-Tetracyanoquinodimethane (TCNQ) (Fig. 1) is a versatile electron acceptor molecule which is used as a building block for a number of functional materials and molecular assemblies.[1-12] TCNQ has been extensively used as the component of organic charge-transfer salts having high electrical conductivity.[1-8] There are a number of papers which study the structure and electronic state of TCNQ and the anion radical $\text{TCNQ}^{\bullet-}$ since 1960s.[13-22] The understanding of photophysics of TCNQ is of potential importance to apply TCNQ to multifunctional materials which have both electrical conductivity and photoluminescence properties.[13] Previous experimental studies showed that the fluorescence quantum yield (QY) of both TCNQ and the anion radical $\text{TCNQ}^{\bullet-}$ is close to zero.[14-16] A main deactivation process of TCNQ in acetonitrile was ascribed to efficient internal conversion (IC) to the ground state.[14] TCNQ derivatives which showed weak fluorescence were also reported.[23]

We have recently reported that the neutral TCNQ emits blue fluorescence with a moderate QY of ca. 0.1 in hexane.[13] The fluorescence of TCNQ showed an acute response to subtle changes in the polarity of solvent, and decreased with increasing solvent polarity. We suggested that an intramolecular charge transfer (ICT) state or a triplet state is related to the excited state dynamics of TCNQ in solutions. Detailed spectroscopic characterization of the isolated TCNQ monomer in the gas phase has been reported recently with laser-induced fluorescence (LIF) and dispersed fluorescence (DF) spectroscopy.[24] The LIF spectrum, which corresponds to the absorption spectrum in the gas phase, showed prominent vibrational progressions and combination bands on a relatively weak 0–0 origin band. Although fluorescence lifetime excited at the origin band was single exponential with 220 ns, the fluorescence excited at the vibronic bands exhibited bi-exponential decay and drastic energy dependence of the lifetime.

The DF spectrum also exhibited vibrational progression of a couple of normal modes in the ground state. An intensity pattern of the DF spectrum was in good agreement with that obtained for solutions.[13,24] These spectra implied that there is a significant deformation of the molecular structure among the excited state and the ground state of TCNQ in the gas phase.

Here, we report fluorescence measurements in polymer matrices to clarify the contribution of the structural deformation in the excited state dynamics of TCNQ in condensed phase. When temperature is changed across glass transition temperature (T_g), the phase of polymer changes between the rubber state and the glass state. Rigidity of polymers, in general, shows a marked change between these two states. Rearrangement of polymer chains to be adapted to the structural deformation of TCNQ is suppressed in the rigid glass state in comparison to the rubber state.[25,26] Therefore, the fluorescence intensity is expected to show variation, when the temperature is changed across T_g . We use three different polymers, poly(methyl acrylate) (PMA), poly(vinyl acetate) (PVAc), and poly(methyl methacrylate) (PMMA) (Fig. 1) which have different T_g to gain understanding of a relation between the rigidity and the fluorescence intensity change.

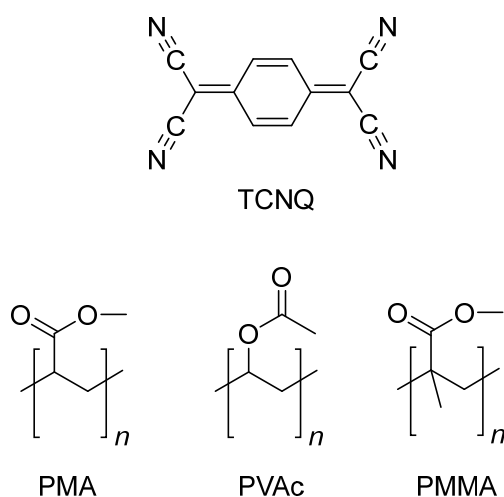


Figure 1. Structures of TCNQ and polymers used in this work.

2. Experimental methods

TCNQ (Tokyo Chemical Industry) was recrystallised with acetonitrile and washed with benzene. Solution of PMA (Aldrich, average molecular weight of 40000, the glass transition temperature $T_g = 9$ °C) in toluene was added to cold hexane to precipitate the polymer, which was then collected from the solution and dried in vacuum to remove the solvents. PMMA (Aldrich, average molecular weight of 120000) was purified by a precipitation method using benzene and methanol. PVAc (Acros organics, average molecular weight of 170000) was used without purification. The polymer (0.34 g) and TCNQ (0.3 mg) were dissolved in dichloromethane (2-3 mL). Thin polymer films containing TCNQ were prepared with a spin coating technique using the polymer solution on slide glass substrates. The substrate was put in an optical cell which was surrounded by a water jacket using a coolant. The temperature of the film was controlled by setting the temperature of the coolant. Measurement was started from +60 °C, and the temperature was decreased to -25 °C. The optical cell was purged with Ar gas. Photobleaching of the emission of TCNQ was carefully suppressed by making duration of photoirradiation to take the spectra as short as possible, and the intensity of photoexcitation as weak as possible by using a neutral density optical filter, respectively. We checked negligible contribution of photobleaching in the measurement of the temperature dependence of fluorescence intensity.

3. Results and discussion

Absorption spectrum of TCNQ in PMA at room temperature is shown in Figure 2. The absorption maximum was observed at 403 nm, and there is a vibronic band at ca. 380 nm. The overall band shape is similar to that observed in chloroform and dichloromethane with

moderate polarity.[13] Fluorescence spectra taken at temperatures in the range from -25 to $+60$ °C are also shown in Fig. 2. The sample was excited at 403 nm for all the temperatures. The fluorescence maxima were observed at 475 nm at temperatures above 28 °C. Slight blue shift of the maximum to 472 nm was observed at lower temperatures. The fluorescence intensity decreased with the increase in temperature, becoming nearly zero at 60 °C. We did not observe obvious change in the bandshape of the fluorescence spectra with the change in temperature.

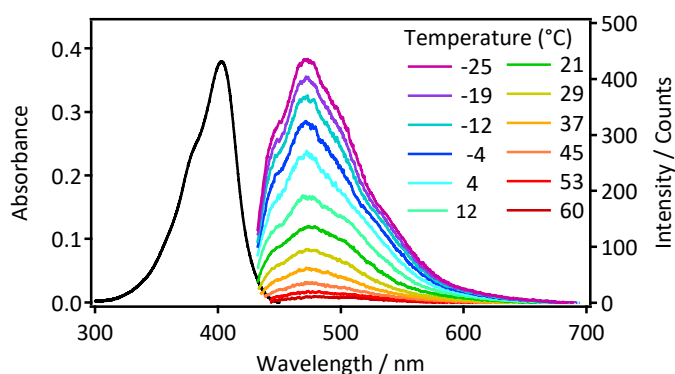


Figure 2. Absorption spectrum at room temperature, and fluorescence spectra of TCNQ dispersed in PMA observed at temperatures from -25 to 60 °C.

Absorption and fluorescence spectra for TCNQ dispersed in PMMA are shown in Fig. 3. The absorption maximum at room temperature was observed at 401 nm. The bandshape of the absorption spectrum is similar to that for the PMA film. The fluorescence maximum was 472 nm above 28 °C, shifted to 470 nm at lower temperatures. The bandwidth and the bandshape of the fluorescence spectra at every temperatures were similar to each other. Although the fluorescence intensity decreased with the increase in temperature, the degree of the decrease at higher temperatures clearly diminished in comparison with that for PMA.

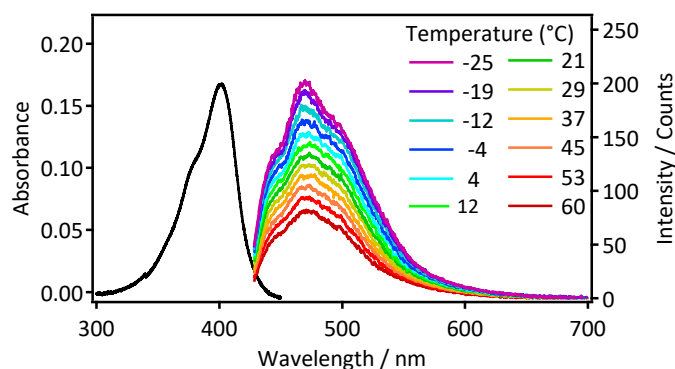


Figure 3. Absorption spectrum at room temperature, and fluorescence spectra of TCNQ dispersed in PMMA observed at temperatures from -25 to 60 $^{\circ}\text{C}$.

Absorption and fluorescence spectra for TCNQ dispersed in PVAc are shown in Fig. 4. The absorption maximum at room temperature was observed at 401 nm. The bandshape of the absorption spectrum is similar to those for the other polymers. The fluorescence maximum was 476 nm at 52 $^{\circ}\text{C}$, shifted to 472 nm at lower temperatures. The bandwidth of the fluorescence spectra hardly changed in the range of temperatures investigated in this work. The fluorescence intensity decreased with the increase in temperature. The degree of the decrease in the fluorescence intensity with the increase of temperature was in-between of those for PMA and PMMA.

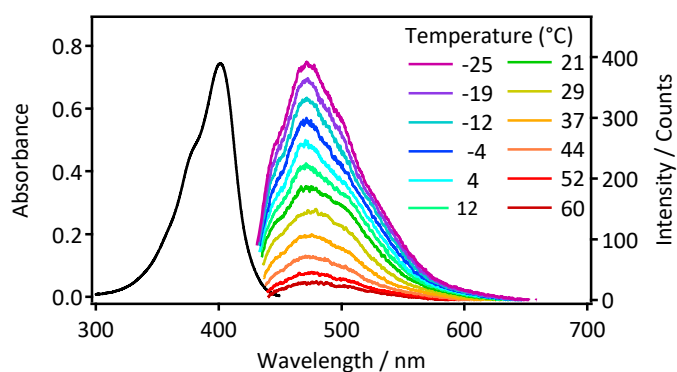


Figure 4. Absorption spectrum at room temperature, and fluorescence spectra of TCNQ dispersed in PVAc observed at temperatures from -25 to 60 $^{\circ}\text{C}$.

The PMA film shows the lowest glass transition temperature $T_g \approx 9^\circ\text{C}$ among the polymers used in this work.[27] The T_g of the PVAc film is in the range between $30\text{--}35^\circ\text{C}$.[28-30] These two polymers are in the rubber state above the T_g , and in the amorphous glass state below the T_g . Accordingly, the rigidity of the polymer matrix surrounding TCNQ is expected to change across the T_g . The T_g of PMMA is ca. 105°C .[29,30] The PMMA does not show the glass transition and is in the glass state in the range of temperatures investigated in this work. Therefore, we can assume that the rigidity of the PMMA matrix does not change largely in this work.

The integral of the fluorescence spectra as a function of temperature is shown in Fig. 5a. At the lowest temperature in the measurement, all of the polymers were in the glass state. The experimentally-observed fluorescence intensity varied according to the difference in QY in each polymers and the thickness of the films. For the sake of the comparison of the temperature dependence of fluorescence intensity among the different polymers, the fluorescence intensity was normalized to that at the lowest temperature. This means that we take the values of the fluorescence intensity for the polymers in the glass state at the lowest temperature as the standard measures of the fluorescence intensity.

The negative slopes of the normalized curves indicate that the fluorescence intensity decreases by increasing the temperature. The curve for the PMMA film showed a monotonic change over the temperatures used in this work. For the PMA film, the slope of the curve became steeper near the T_g than that at the lower temperatures, and an inflection point appeared. At the temperatures above the T_g , the slope of the curve is restored to that at the lower temperatures. We observed a similar feature on the curve for the PVAc film at the corresponding T_g . The first derivatives of the curves are shown in Fig. 5b for the sake of the illustration of the slope change at T_g . The first derivative for the PMA film clearly showed a

minimum at the T_g , representing the steep change and the corresponding sharp decrease in the fluorescence intensity. There was also a dip at the T_g on the first derivative for the PVAc film. The first derivative for the PMMA film was nearly flat in the range from -10 to 50 °C. The value of the integral of the fluorescence spectrum which was obtained just before starting the sequence of the measurement of temperature dependence for the PMA film is indicated on Fig. 5a. This value was nearly reproduced during the course of the measurement, illustrating that the change in the fluorescence intensity by changing the temperature was nearly reversible.

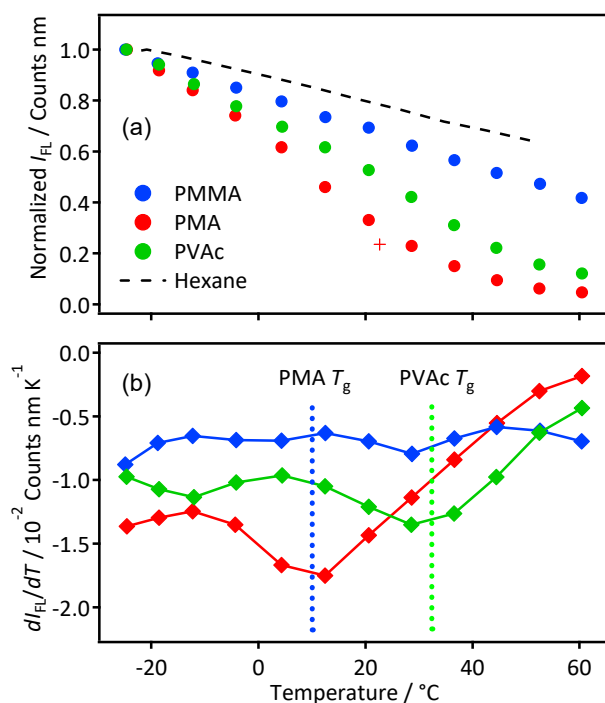


Figure 5. (a) The integral of the fluorescence spectra (I_{FL}) normalized at -25 °C as a function of temperature (T). (+) The value of I_{FL} which was obtained just before starting the sequence of the measurement of temperature dependence for PMA. (b) First derivatives of the I_{FL} . T_g of PMA and PVAc are indicated by the dotted lines.

We now discuss whether the change in the fluorescence intensity originates from the change in the absorption spectrum. Although we could actually measure the absorption spectra only at

room temperature, the fluorescence excitation spectra at different temperatures were measured instead of the absorption spectra (Fig. 6). The shapes of the spectra both at the low temperature and room temperature were similar to each other. This result demonstrates that the absorption spectra were nearly the same when the temperature was varied. The rate of the excitation, namely the transition probability, of TCNQ was also nearly the same at all the temperatures, because the concentration of TCNQ, the excitation light intensity, and the absorbance were constant. Therefore, the main origin of the change in the fluorescence intensity as a function of temperature in Fig. 5 must be the change in the fluorescence QY. For the PVAc film in Fig.6, the shape of the excitation spectrum was slightly distorted in comparison with that of the absorption spectrum. This is explained by the inner filter effect,[31,32] because the absorbance of the sample used in this measurement was 1.2 at the absorption maximum.

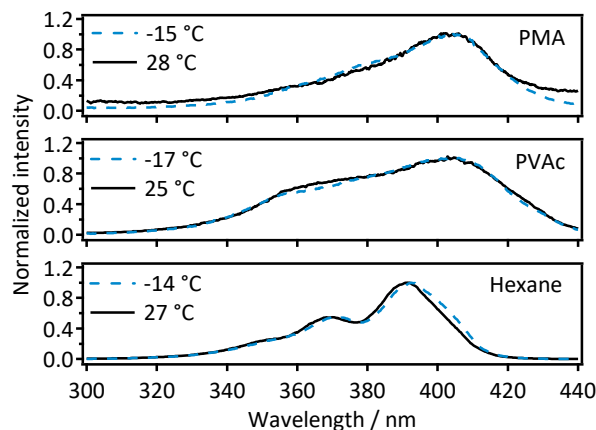


Figure 6. Fluorescence excitation spectra for PMA, PVAc, and hexane obtained by monitoring 470, 470, and 466 nm, respectively. The intensities of all of the spectra were normalized to those at the excitation maximum.

The fluorescence QY is given by the ratio between the radiative decay rate (k_R) and the sum of k_R and the nonradiative decay rate k_{NR} . The k_R is generally regarded as independent on temperature in such narrow temperature range as used in this work. The slope of the curve in

Fig. 5a is determined by the variation of the k_{NR} as a function of temperature. The fluorescence QY decreases with the increase in temperature when the nonradiative decay process of the photoexcited TCNQ is thermally activated process. We investigated whether the decrease in the fluorescence QY is observed in a material other than the polymers. The fluorescence spectra in hexane are shown in Fig. 7. The hexane solution was in the liquid phase in the range of temperatures used in this work, and the change in viscosity was not significant. The shape of the fluorescence excitation spectrum, which reflected the shape of the absorption spectrum, hardly changed at the different temperatures (Fig. 6). The integral of the fluorescence spectrum as a function of temperature is appended in Fig. 5a. The fluorescence intensity monotonically decreased by increasing the temperature, and the main origin of this observation must be the change in the fluorescence QY. One can conclude that the thermally-activated nonradiative decay process is the intrinsic property of TCNQ irrespective of the surrounding materials of TCNQ.

Although the PMA and PVAc films exhibit the glass transition, the PMMA film keeps the glass state in the whole range of the temperature. The monotonic change of the fluorescence intensity for the PMMA film (Fig. 5a) shows that the k_{NR} monotonically changes with temperature, as observed in hexane. It is likely that the nonradiative decay process which is thermally activated irrespective of the rigidity also exists in the other polymers. Further discussion on the detail of the k_{NR} is outside the scope of the present paper. We can employ the data for the PMMA film as the reference to describe the temperature dependence of the k_{NR} independent of the glass transition of the matrix.

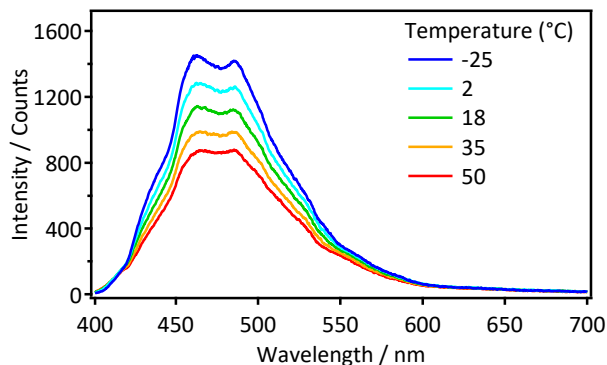


Figure 7. Fluorescence spectra of TCNQ in hexane observed at temperatures from -25 to 50 °C. The excitation wavelength was 391 nm.

The shape of the first derivative of the fluorescence intensity versus temperature was linked to the presence of the glass transition (Fig. 5). It is unlikely that there are specific interactions such as the hydrogen bonding or the CT interaction between TCNQ and the polymers used in this work. The concentration of TCNQ and the solvent used to prepare the films were identical for all of the polymers (see experimental section). The observed difference in the first derivatives can be ascribed to the difference in the physical properties of the polymers.

For the PMA and PVAc films, the rigidity of the surrounding of TCNQ largely varies when the temperature changes across the T_g . In the rubber state at temperatures higher than T_g , we can expect that the structural deformation of TCNQ occurs more efficiently in comparison to the glass state. If the glass transition is absent for the PMA and PVAc films, we should expect the flat derivative which is similar to the PMMA film (Fig. 5b). Actually, the change in the derivatives at the T_g for the PMA and PVAc films indicates that the increasing rate in k_{NR} per a unit temperature at the T_g is larger than that expected for the films in the glass state. When the nonradiative decay process in the excited state of TCNQ is accompanied by the structural deformation, we can expect larger k_{NR} in the rubber state than in the glass state even at the same

temperature. Therefore, the marked change in fluorescence QY at the T_g is consistent with the nonradiative decay process accompanied by the structural deformation.

In the previous study, we have shown that the fluorescence QY is highly sensitive to the polarity of the solvent.[13] The fluorescence QY in solution as a function of $f(D)$ in the range from 0.5 to 0.85 has already been evaluated by using the mixture of hexane and dichloromethane elsewhere,[13] where $f(D)$ is the Onsager polarity function defined by $f(D) = 2(D - 1)/(2D + 1)$ and D is the dielectric constant of the solvent.[33] The $f(D)$ of the solution was changed in this range by changing the volume fractions (x_{DCM}) of the dichloromethane in the mixture. The result is partly reproduced in Fig. 8.

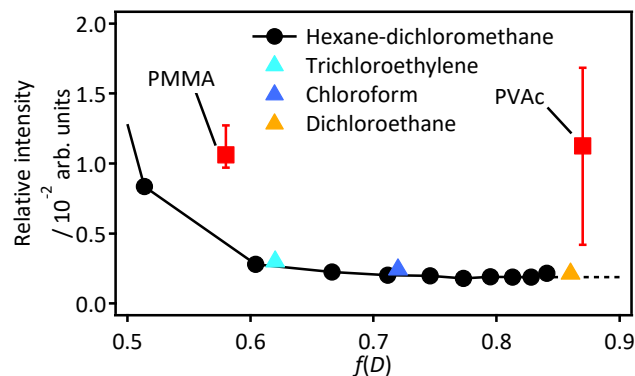


Figure 8. Fluorescence intensity relative to the hexane solution as a function of $f(D)$.

The dielectric constant D_{MIX} of the binary mixture was approximately calculated as $D_{MIX} = (1 - x_{DCM})D_{HEX} + x_{DCM}D_{DCM}$, where D_{HEX} and D_{DCM} are the dielectric constants for hexane and dichloromethane, respectively.[33] The fluorescence spectra were excited at the corresponding absorption maxima. The fluorescence intensity in Fig. 8 was obtained by dividing the intensity of the fluorescence maximum by the absorbance at the absorption maximum for each of compositions of the binary mixture, and then normalized to that for

hexane. The curve in Fig. 8, therefore, represents the change in the fluorescence QY relative to that for hexane. Note that the fluorescence QY in pure hexane was determined to be 0.11.[13] The fluorescence QY for the binary mixture decreased with the increase in $f(D)$, and became nearly constant at $f(D) > \text{ca. } 0.7$. The fluorescence intensity for trichloroethylene, chloroform, and dichloroethane are also plotted at the corresponding values of $f(D)$. For both of the binary mixture and the pure solvents, the fluorescence QY obeys a universal curve. This result indicated that the $f(D)$ is a good parameter with which to correlate to the fluorescence QY of TCNQ.[13]

We can discuss the effect of the rigidity of the medium by comparing the fluorescence QY between the solvents and the polymers which have the similar polarity to one another. For the PMMA film and the PVAc film, we obtain $f(D) = 0.58$ and 0.87 with the reported values of $D \approx 3.1$ and 11 , respectively.[30,34] The experimental error in Fig. 8 was estimated from the measurements of ten and eight different samples for the PMMA film and the PVAc film, respectively. On the average, the fluorescence QY of TCNQ in the polymers was six times as large as that in the solvents having the similar $f(D)$. This result indicates that the fluorescence QY increases in more rigid environments, consistent with the scenario that the nonradiative decay process from the emissive state is accompanied by the structural deformation.

It is known that the fluorescence dynamics of molecules which have an intramolecular charge-transfer state (ICT) in the excited state are sensitive to the solvent polarity.[31] The marked solvation effect on the fluorescence QY of TCNQ can also be explained by the existence of a dark ICT state which is coupled with the fluorescence emissive state.[13] The formation of a twisted ICT (TICT) state is often argued to interpret photophysical property of some fluorophores.[31,32] When the rigidity of microenvironment surrounding TCNQ is increased, the relaxation rate from the emissive state to the TICT state can be decreased, possibly leading to the increase in the fluorescence QY. However, there has been no evidence

by experimental observation nor theoretical calculation for the existence of a TICT state to the best of our knowledge. Recently, the fluorescence lifetime of isolated TCNQ in a cold gas phase was measured using the high-resolution laser excitation.[24] The fluorescence lifetime excited at the origin band of the S_1 - S_0 transition was 220 ns. This lifetime is more than 40 times longer than the radiative lifetime estimated from the S_1 - S_0 oscillator strength reported by Khvostenko [35]. This unusually long fluorescence lifetime in the gas phase implied that a mixing of the S_1 state with the T_1 state or an ICT state. We need to await further experimental and theoretical studies to characterize the electronic state to which the nonradiative decay occurs from the emissive state.

4. Conclusions

The dependence of the fluorescence QY of TCNQ on the rigidity of microenvironment surrounding the molecule was investigated. The three different polymers which have different T_g were compared as the matrices. The glass transition is absent for the PMMA film at the temperatures used in this work. The fluorescence QY of the PMMA film showed a nearly monotonic decrease with the increase in temperature. Although the fluorescence QY was also decreased for the PMA and PVAc films with the increase in temperature, the slope of the fluorescence QY versus temperature became steeper at the corresponding T_g . This result shows that the decreasing rate of the fluorescence QY per a unit temperature is larger in the rubber state than in the glass state. The fluorescence QYs in the polymers were larger than those in the solvents having the similar $f(D)$. These results demonstrate that the fluorescence QY is increased with the increase in the rigidity of microenvironment. We conclude that the main nonradiative decay process from the fluorescence emissive state of TCNQ is accompanied by the structural deformation.

Acknowledgments

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