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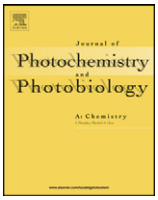

Fluorescence properties of ion pair charge transfer complex with bithiophene group

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ABSTRACT

The fluorescence properties of ion pair charge transfer (IPCT) complex with bithiophene group were studied by steady-state and time-resolved measurements in various solvents. The photophysical properties of 5,5′-di(4-pyridyl)-2,2′-bithiophene (DPBT) were identical to the unsubstituted bithiophene except for the peak wavelength. The absorption of polymeric 5,5′-di(4-pyridiniumyl)-2,2′-bithiophene (PBT^{2+}) salts showed both the locally excited state (LE) and intramolecular charge transfer (ICT) bands in all solvents studied. In less-polar solvents such as cyclohexane and toluene, absorption spectra showed an IPCT band in addition to the LE and ICT bands. The fluorescence spectra of polymeric PBT^{2+} salts showed dual emission which originated from the LE and ICT states in polar solvents. The ICT fluorescence lifetime strongly depends on the solvent polarity. The fluorescence from the PBT^{2+} salts was effectively quenched by their counter ion in less-polar solvent. These results indicate that the counter halide anion affects on the excited-state relaxation process.

1. Introduction

Thiophenes have remarkable optical and electrochemical properties in π-conjugated polymers. Polythiophenes and oligothiophenes have been extensively studied not only in materials chemistry such as organic light emitting diodes [1], field effect transistor [2], and photovoltaic cells [3], and non-linear optics and chemical sensor devices [4], but also the fundamental chemistry, photochemistry and electrochemistry. Therefore it is essential to study the ground- and excited-state properties of thiophene derivatives by steady-state spectroscopy and time-resolved measurements. Lap et al. reported femtosecond transient absorption spectroscopy of oligothiophene in solutions [5,6]. Picosecond fluorescence spectroscopy was reported by several groups [7–9]. The oligothiophene has lower two (ππ*) states, their energy states depend on the number of the thiophene rings [7]. The fluorescence lifetime and fluorescence quantum yield increased with ring number, which is mainly caused by the decrease of nonradiative decay [8]. The changes of electronic state affect the excited-state dynamics and electronic properties, which control the charge transport and optical processes in polythiophenes.

The π-conjugated molecular systems are also important to all-optical information processing based on the organic materials because the optical telecommunication wavelength locates in the near-infrared (NIR) region. We have been studying the ion pair charge transfer (IPCT) complexes based of bipyridinium derivatives to achieve such purposes [10]. Incorporation of conjugated chromophores between two pyridinium units has been designed and synthesized based on concepts that π-conjugation throughout three or four chromophores upon one-electron reduction is effective to achieve a wide range absorption extending from visible to the NIR region. The expanded π-electron IPCT complexes with fluorene chromophore between two pyridinium units showed ultra fast transient absorption change in the NIR wavelength region, which originates from transitory expansion of a π-electronic system by photoinduced electron transfer and reverse reactions between redox-active ion pairs within ps time region [11]. In addition the IPCT complexes show CT fluorescence which is attributed to transitions between the ion pairs making CT interactions [12]. We also reported the first example of fluorescence from IPCT complexes of 4,4′-bipyridinium and tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ion in organic solution [13]. The IPCT fluorescence properties strongly depend on the environmental conditions: phase, solvent, temperature and counter ion.

Recently we designed and synthesized polymeric 5,5′-di(4-pyridiniumyl)-2,2′-bithiophene (PBT^{2+}) salts as shown in Fig. 1. The extended viologen using thiophene units were reported previously [14–16]. These papers however mainly discussed on the

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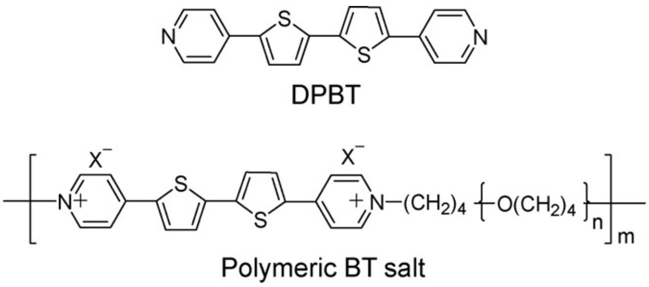

Fig. 1. Molecular structures of DPBT and polymeric BT salt.

photo-electrochemical properties. In this paper we focus on the fluorescence properties of $PBT^{2+}2Br^-$ and $PBT^{2+}2I^-$. The fluorescence properties of 5,5′-di(4-pyridyl)-2,2′-bithiophene (DPBT) was also investigated as a reference compound.

2. Experimental

The DPBT, $PBT^{2+}2Br^-$ and $PBT^{2+}2I^-$ were synthesized as reported in a separate paper [17]. All solvents (Dojin, Wako and Nacalai tesque) for the spectroscopic measurements were of spectroscopic or luminasol grade and were used without further purification. UV–vis absorption spectra were measured by Hitachi U-4100 spectrometer. Fluorescence spectra were recorded by Hitachi F-4500 spectrophotometer. The concentrations of chromophore units for DPBT, $PBT^{2+}2Br^-$ and $PBT^{2+}2I^-$ were less than 1×10^{-5} mol dm^{-3}. The fluorescence quantum yields Φ_f were determined by quinine bisulfate in 0.05 mol dm^{-3} sulphuric acid as a standard ($\Phi_s = 0.546$). The Φ_f-values were estimated by the following relation:

$$\Phi_f = \Phi_s \frac{F_f}{F_s} \frac{1 - 10^{-A_s}}{1 - 10^{-A_f}} \frac{n_f^2}{n_s^2} \qquad (1)$$

where F is the corrected fluorescence peak area, A the absorbance at the excitation wavelength, n the refractive index of the solvent used, Φ the fluorescence quantum yield and subscripts ‘f’ and ‘s’ are the sample and the standard, respectively. Fluorescence lifetimes were measured by a single photon counting method using a streakscope (Hamamatsu Photonics, C4334-01) [18]. The sample solutions were excited with SHG of a Ti:sapphire laser (Spectra-Physics, Tsunami, fwhm: 1.5 ps) equipped with a pulse selector and a harmonic generator. All experiments were carried out at room temperature.

3. Results and discussion

3.1. Absorption and fluorescence spectra of DPBT

Fig. 2 shows the UV–vis absorption and fluorescence spectra of DPBT in DMF solution. DPBT has an absorption band peaked at λ = 385 nm and weak shoulder at λ = 410 nm in toluene solution, which is identical to the previous report [14]. The molar absorption coefficient of DPBT in DMF solution is 32,190 M^{-1} cm^{-1} at 385 nm, which means this band can be assigned to π–π* transition. The absorption peak shifts to red compared with unsubstituted bithiophene [7,19]. The fluorescence spectrum of DPBT has a vibrational structure at λ = 430 and 450 nm and shoulder at λ = 490 nm, meaning that bithiophene rings of DPBT are relatively planar and rigid, which was reported in the case of terthiophenes [20]. The Stokes shift was 1350 cm^{-1} in toluene solution, which was estimated from the wavenumber of shoulder in the absorption band and first vibrational band of fluorescence spectrum. The absorption and fluorescence spectra showed mirror image. It is suggested that the electronic structural change scarcely occurred in the excited state. The fluorescence quantum yield (Φ_f) of DPBT was estimated to be 0.1. The fluorescence lifetime (τ) of DPBT was estimated to be τ = 280 ps with a single exponential function. The fluorescence rate constant (k_f) is estimated as 3.5×10^8 s^{-1} from $k_f = \Phi_f \tau$. The intrinsic radiative lifetime τ_f^0 was calculated from the absorption spectra using the modified Strickler–Berg relation [21]. The k_f is estimated to be 2.97×10^8 s^{-1} from τ_f^0. The k_f value from the fluorescence lifetime and quantum yield is comparable to the calculated value. We measured the absorption, fluorescence spectra and fluorescence lifetime of DPBT in various solutions. No remarkable changes of absorption and fluorescence spectra together with fluorescence lifetime were observed. These findings indicate that DPBT has mainly π–π* character rather than intramolecular charge transfer (ICT) character.

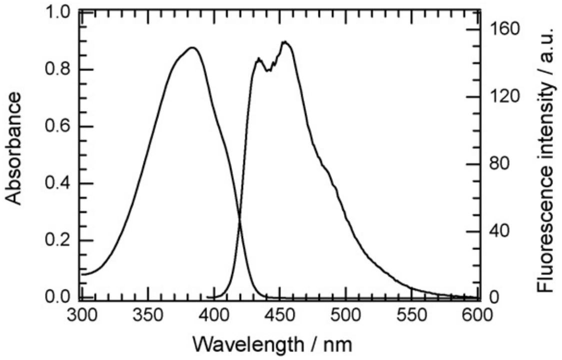

Fig. 2. Absorption and fluorescence spectra of DPBT in DMF solution. The fluorescence spectrum was excited at λ = 365 nm.

3.2. Absorption spectra of polymeric PBT salts

We measured absorption spectra of the polymeric IPCT complexes. Fig. 3 shows absorption spectra of $PBT^{2+}2Br^-$ in various solvents. The well-defined absorption band around λ = 450 nm was observed in addition to the absorption band of DPBT around λ = 380 nm. The absorption band around λ = 380 nm can be assigned to the LE band of the bithiophene moiety with π–π* character. The pyridine rings at both sides of bithiophene possess electron accepting ability by the quarternization. The new absorption band is most likely due to ICT absorption band between bithiophene as a donor and pyridinium part as an acceptor. This assignment will be discussed later including the fluorescence properties. Fig. 4 shows the absorption spectra of $PBT^{2+}2I^-$ in various solutions. The two absorption bands at λ = 385 nm and shoulder at λ = 410 nm were observed in all solutions, which is similar to the absorption character of $PBT^{2+}2Br^-$. The absorption spectra of $PBT^{2+}2Br^-$ and $PBT^{2+}2I^-$ in cyclohexane indicated absorption tailing up to λ = 700 nm, which are relatively weak as compared with LE and ICT bands. Eigen and Fusso formulated the association constant of ion pairs by electrostatic interaction in a dielectric constant of solvent [22,23]. It is suggested that the extent of ion pairing increases in less-polar solvents and at low ionic strength. Thus $PBT^{2+}2Br^-$ and $PBT^{2+}2I^-$ were dissolved most probably as contact ion pairs in cyclohexane. These findings indicate that the absorption at longer wavelength region can be assigned to ion pair charge transfer (IPCT) complexes between the counter anions to PBT^{2+}. The spectral shape of $PBT^{2+}2I^-$ in DMF solution is unclear in comparison with other solutions.

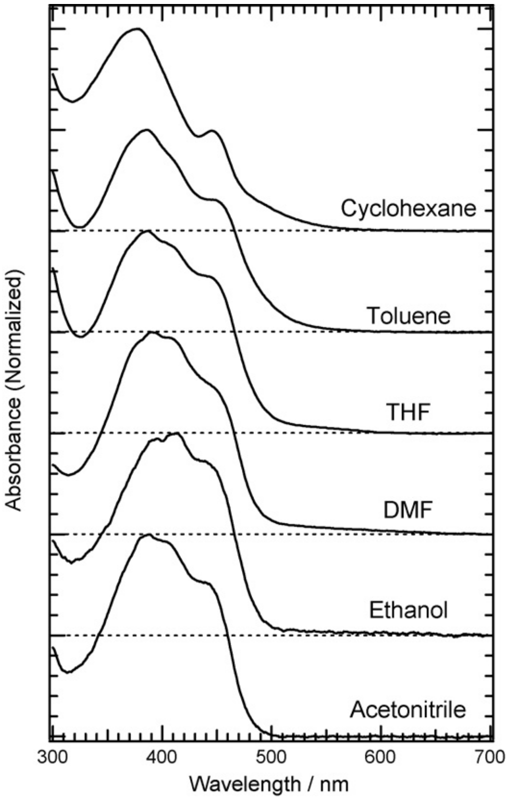

Fig. 3. Absorption spectra of $PBT^{2+}2Br^{-}$ in various solvents.

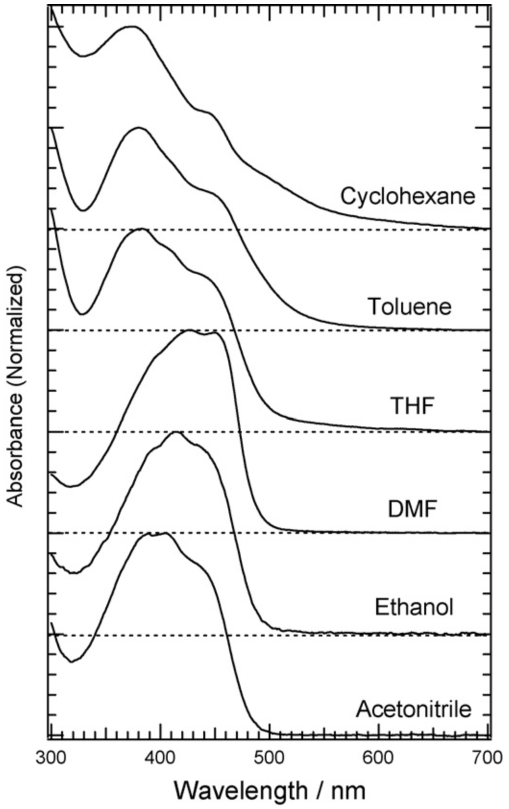

Fig. 4. Absorption spectra of $PBT^{2+}2I^{-}$ in various solvents.

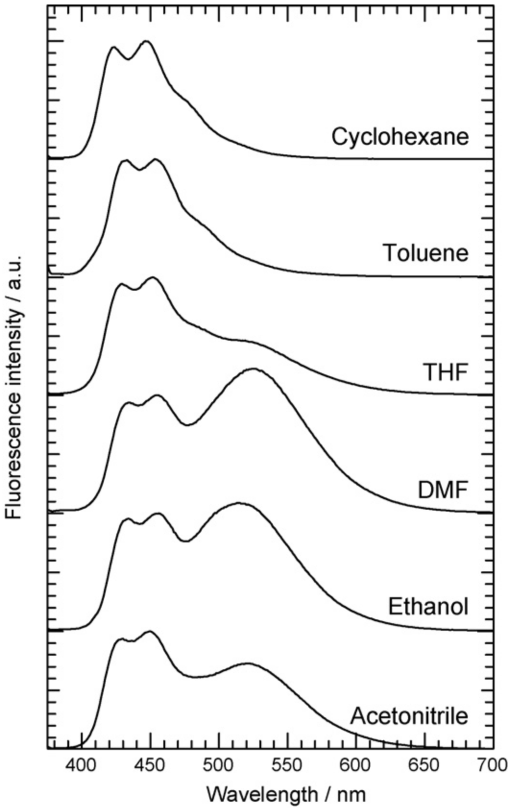

Fig. 5. Fluorescence spectra of $PBT^{2+}2Br^{-}$ in various solvents. The excitation wavelength was 365 nm.

3.3. Fluorescence properties of polymeric PBT salts

Figs. 5 and 6 show fluorescence spectra of $PBT^{2+}2Br^{-}$ and $PBT^{2+}2I^{-}$ in various solvents, respectively. The fluorescence spectra of both $PBT^{2+}2Br^{-}$ and $PBT^{2+}2I^{-}$ in cyclohexane and toluene shows two vibrational structures around $\lambda = 430$ and 450 nm, which are almost identical to the fluorescence of DPBT. The fluorescence excitation spectra monitored at $\lambda = 500$ nm fit to the absorption spectra of the LE absorption with $\pi\pi^*$ character ($\lambda = 380$ nm) as described in a previous section. This band can be assigned to the LE band of bithiophene. A new structureless emission band around $\lambda = 530$ nm built up with increasing the solvent polarity. The fluorescence excitation spectra in polar solvents from THF to acetonitrile agree with the absorption band around $\lambda = 450$ nm corresponding to ICT absorption band. We attribute this emission band to a species having pronounced ICT character. Thus the polymeric PBT^{2+} has a potential minimum of the CT state both in the ground and excited states. The IPCT absorption was observed in cyclohexane and toluene solution. However the IPCT fluorescence was not observed in such solution. In the case of IPCT with halide ions, the IPCT fluorescence scarcely observed at room temperature [10]. These findings strongly supported that the polymeric PBT salts dissolved as contact ion pair in non-polar solvents.

To investigate the fluorescence dynamics of the polymeric PBT^{2+} salts, fluorescence decay profiles in different solvents were measured. The fluorescence decay around $\lambda < 430$ nm shows single exponential decay about 0.3 ns in less-polar solvent (cyclohexane and toluene), which is similar to the LE fluorescence decay time constant of DPBT as shown in Tables 1 and 2. Thus, the fluorescence decay time constants about 0.3 ns around $\lambda < 430$ nm can be assigned to the LE fluorescence lifetime. The fluorescence decay profiles in polar solvent could not be separated between the LE and ICT fluorescence because the ICT fluorescence is much stronger

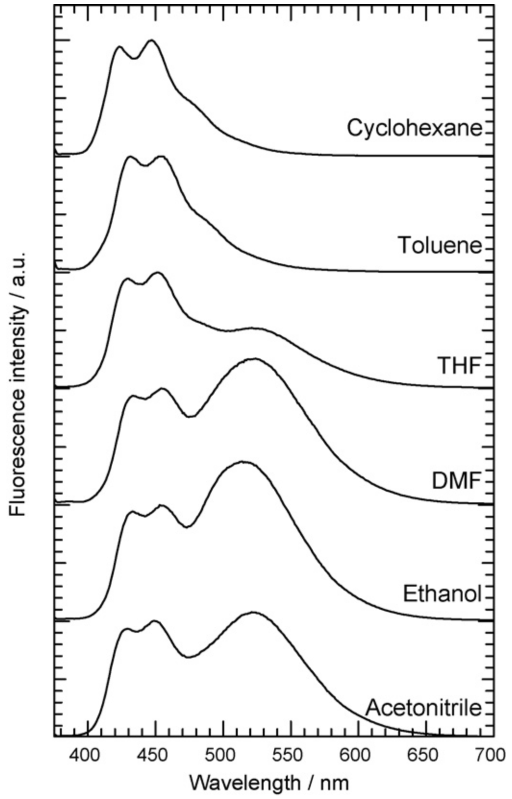

Fig. 6. Fluorescence spectra of $PBT^{2+}2I^-$ in various solvents. The excitation wavelength was 365 nm.

Table 1
Fluorescence properties of $PBT^{2+}2Br^-$ in various solvents.

Solvent	Δf[a]	ϕ_f[b]	Fluorescence lifetime			
			$\lambda < 430$ nm	$\lambda > 450$ nm		
			τ (ns)	τ_1 (ns)	τ_2 (ns)	τ_{avg} (ns)
Cyclohexane	−0.00131	0.062	0.31	0.16	0.98	0.30
Toluene	0.01314	0.070	0.28	0.32	1.42	0.58
THF	0.14816	0.103		0.36	2.36	1.82
DMF	0.16690	0.141		–	2.39	2.39
Ethanol	0.20959	0.172		–	2.23	2.23
Acetonitrile	0.30457	0.156		–	2.38	2.38

[a] Solvent parameter: $\Delta f(\varepsilon, n) = ((\varepsilon - 1)/(2\varepsilon + 1)) - ((n^2 - 1)/(2n^2 + 1))$.
[b] Total fluorescence quantum yield both the LE and ICT fluorescence.

Table 2
Fluorescence properties of $PBT^{2+}2I^-$ in various solvents.

Solvent	Δf[a]	ϕ_f[b]	Fluorescence lifetime			
			$\lambda < 430$ nm	$\lambda > 450$ nm		
			τ (ns)	τ_1 (ns)	τ_2 (ns)	τ_{avg} (ns)
Cyclohexane	−0.00131	0.045	0.31	0.15	0.98	0.26
Toluene	0.01314	0.048	0.33	0.25	1.44	0.48
THF	0.14816	0.092		0.45	2.32	1.59
DMF	0.16690	0.162		–	2.16	2.16
Ethanol	0.20959	0.194		–	2.18	2.18
Acetonitrile	0.30457	0.185		–	2.19	2.19

[a] Solvent parameter: $\Delta f(\varepsilon, n) = ((\varepsilon - 1)/(2\varepsilon + 1)) - ((n^2 - 1)/(2n^2 + 1))$.
[b] Total fluorescence quantum yield both the LE and ICT fluorescence.

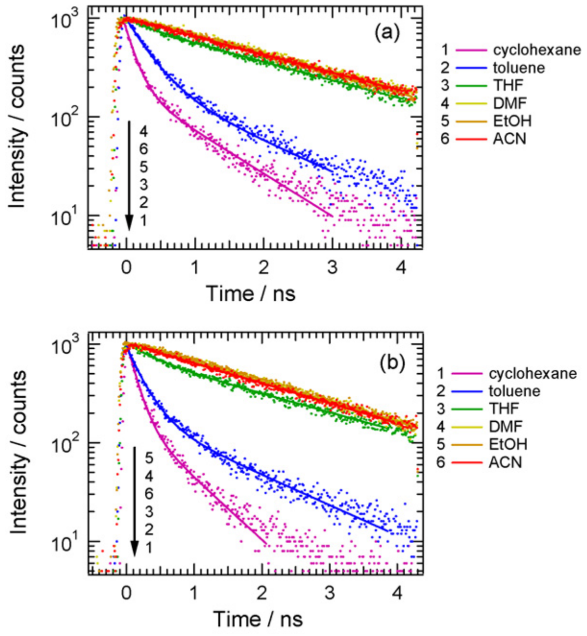

Fig. 7. Fluorescence decay profiles of $PBT^{2+}2Br^-$ (a) and $PBT^{2+}2I^-$ (b) in various solvents excited at $\lambda = 420$ nm laser pulse monitored at $\lambda > 500$ nm. Solid lines indicate the fitting curves based on the exponential function.

than the LE band in polar solvents and the ICT fluorescence tail was overlapped at the LE band. Thus, the apparent LE fluorescence behavior cannot be observed by time-resolution of the present system is about 300 ps. Fig. 7 shows the fluorescence decay profiles of $PBT^{2+}2Br^-$ and $PBT^{2+}2I^-$ excited at $\lambda = 420$ nm laser pulse and monitored at $\lambda > 500$ nm. It is clearly shown that the decay is single exponential in polar solvents, but it becomes faster and non-single exponential in less-polar solvents. Tables 1 and 2 summarized the fluorescence lifetime (τ) of $PBT^{2+}2Br^-$ and $PBT^{2+}2I^-$. In the case of a double-exponential decay, the averaged fluorescence lifetime (τ_{avg}) was calculated by $\tau_{avg} = (A_1\tau_1 + A_2\tau_2)/(A_1 + A_2)$, where A_1 and A_2 are pre-exponential factors. In less-polar solvent such as cyclohexane and toluene, the fluorescence decays show two components, which reproduced as double-exponential function. These faster and slower components probably assigned to the tail of the LE fluorescence and ICT fluorescence quenched by their counter ion, respectively. In polar solvents the fluorescence intensity shows very fast rise and decays with a single exponential function. It is difficult to determine the rise time constant by our experimental setup. These findings indicate that the ICT state is rapidly generated from the LE excited state in polar solvents. In THF having an intermediate-polarity, the fluorescence decay slightly indicates double-exponential decay with a very fast rise component. The fluorescence lifetime of $PBT^{2+}2Br^-$ and $PBT^{2+}2I^-$ was increased about eight times when the solvent changes from cyclohexane to acetonitrile as represented in Tables 1 and 2, respectively. The fluorescence dynamics strongly depends on the solvent polarity. In less-polar solvent, the fluorescence from the PBT^{2+} salts was effectively quenched by their counter ions. Both $PBT^{2+}Br^-$ and $PBT^{2+}I^-$ most probably exist as contact ion pairs in non-polar solvents judged from the absorption spectra. Therefore the excited state of PBT^{2+} is strongly affected by their counter ion. It cannot be neglected the contribution of ICT fluorescence quenching by the counter ion. These results are distinct from the usual CT fluorescence [24]. Beaumont and Davis [25] studied the fluorescence quenching of *N*-methylacridinium ion by a range of counter ions. The quenching efficiency depended on the nature of anions and on solvents. The quenching constant was higher both in less-polar solvents and for those anions with positive redox potentials. In addition, association constants for IPCT complex formation were generally much smaller than the quenching constant which increased with solvent fluidity. From these results it was indicated that the quenching occurred by three distinct mechanisms, static quenching due to IPCT complex formation, further complex formation in the excited state, and collisional quenching [25]. These findings imply decreasing of the fluorescence lifetime and quantum yield of polymeric PBT^{2+} salts in less-polar solvents. Significant difference of fluorescence properties was not observed between $PBT^{2+}2Br^-$ and $PBT^{2+}2I^-$.

On the other hand, it is well known that thiocyanate and halide ions are effective fluorescence quenchers of aromatic molecules [26–29]. The quenching efficiency increases with increasing oxidation potential of the anion. Although the electron transfer from aromatic anion to fluorophore is responsible for quenching, the formation of aromatic radical anion is usually not observed. Watkins et al. [26–28] proposed that the anion enhances the intersystem crossing rate of the fluorophore owing to a perturbation of its lowest energy excited state by excited CT state. Shizuka et al. [30] have examined the effect of quenchers on triplet–triplet absorption spectrum of some aromatic molecules and have determined the rate constants for anion-induced intersystem crossing. The anion-induced intersystem crossing rate constant obeys the heavy atom effects, although the fluorescence quenching increases with increasing oxidation potential of the anion. The electron transfer reaction between neutral fluorophore and anion is responsible for the fluorescence quenching and that the resulting CT complex is effective. Recently Horiuchi and Hiratsuka reported that photodegradation processes from the triplet state of cyanine dyes (salts) in the film was induced by singlet molecular oxygen [31]. They suggested that the relative reactivity of carbocyanine dyes with the singlet molecular oxygen strongly depended on the counterion which induced the heavy atom effects. These findings summarized that the lifetime of the excited singlet state is influenced by both electron transfer and the external heavy atom effects. It is compatible with the electron transfer quenching and the heavy atom effects at PBT^{2+} salts, the effects are indistinguishable. It is found that the halide ions affect on the fluorescence lifetime of the PBT^{2+} salts in less-polar media, which exist as contact ion pair. It will be necessary to measure and to estimate the quantum yield of intersystem crossing in the PBT^{2+} salts for further discussion.

4. Conclusion

The absorption and fluorescence properties of DPBT and polymeric PBT^{2+} salts ($PBT^{2+}2Br^-$ and $PBT^{2+}2I^-$) were studied. The absorption and fluorescence properties of DPBT were identical to that of bithiophene. The absorption of polymeric PBT^{2+} salts showed the LE and ICT band in all solvents. In less-polar solvents such as cyclohexane and toluene absorption spectra further indicated the IPCT band. The fluorescence spectra of polymeric PBT^{2+} showed the dual emission originated from the LE and ICT state in polar solvents. The counter halide anion affects on the excited-state relaxation process in the non- or less-polar solvents.

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