

## 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<sup>2+</sup>) 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<sup>2+</sup> 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<sup>2+</sup> 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.

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### 1. Introduction

Thiophenes have remarkable optical and electrochemical properties in  $\pi$ -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 ( $\pi\pi^*$ ) 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.

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The  $\pi$ -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  $\pi$ -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  $\pi$ -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  $\pi$ -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<sup>2+</sup>) salts as shown in Fig. 1. The extended viologen using thiophene units were reported previously [14–16]. These papers however mainly discussed on the

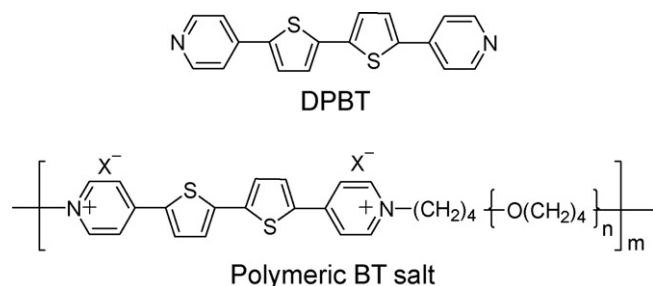


Fig. 1. Molecular structures of DPBT and polymeric BT salt.

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

## 2. Experimental

The DPBT,  $\text{PBT}^{2+}2\text{Br}^-$  and  $\text{PBT}^{2+}2\text{I}^-$  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,  $\text{PBT}^{2+}2\text{Br}^-$  and  $\text{PBT}^{2+}2\text{I}^-$  were less than  $1 \times 10^{-5} \text{ mol dm}^{-3}$ . The fluorescence quantum yields  $\Phi_f$  were determined by quinine bisulfate in 0.05  $\text{mol dm}^{-3}$  sulphuric acid as a standard ( $\Phi_s = 0.546$ ). The  $\Phi_f$ -values were estimated by the following relation:

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

where  $F$  is the corrected fluorescence peak area,  $A$  the absorbance at the excitation wavelength,  $n$  the refractive index of the solvent used,  $\Phi$  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  $\lambda = 385 \text{ nm}$  and weak shoulder at  $\lambda = 410 \text{ nm}$  in toluene solution, which is identical to the previous report [14]. The molar absorption coefficient of DPBT in DMF solution is  $32,190 \text{ M}^{-1} \text{ cm}^{-1}$  at  $385 \text{ nm}$ , which means this band can be assigned to  $\pi-\pi^*$  transition. The absorption peak shifts to red compared with unsubstituted bithiophene [7,19]. The fluorescence spectrum of DPBT has a vibrational structure at  $\lambda = 430$  and  $450 \text{ nm}$  and shoulder at  $\lambda = 490 \text{ nm}$ , meaning that bithiophene rings of DPBT are relatively planar and rigid, which was reported in the case of terthiophenes [20]. The Stokes shift was  $1350 \text{ cm}^{-1}$  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 mir-

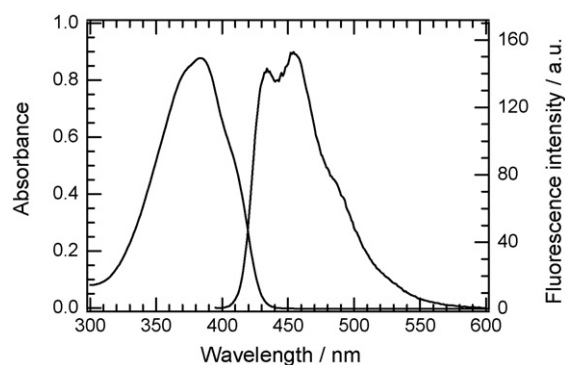


Fig. 2. Absorption and fluorescence spectra of DPBT in DMF solution. The fluorescence spectrum was excited at  $\lambda = 365 \text{ nm}$ .

ror image. It is suggested that the electronic structural change scarcely occurred in the excited state. The fluorescence quantum yield ( $\Phi_f$ ) of DPBT was estimated to be 0.1. The fluorescence lifetime ( $\tau$ ) of DPBT was estimated to be  $\tau = 280 \text{ ps}$  with a single exponential function. The fluorescence rate constant ( $k_f$ ) is estimated as  $3.5 \times 10^8 \text{ s}^{-1}$  from  $k_f = \Phi_f \tau$ . The intrinsic radiative lifetime  $\tau_f^0$  was calculated from the absorption spectra using the modified Strickler-Berg relation [21]. The  $k_f$  is estimated to be  $2.97 \times 10^8 \text{ s}^{-1}$  from  $\tau_f^0$ . 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  $\pi-\pi^*$  character rather than intramolecular charge transfer (ICT) character.

### 3.2. Absorption spectra of polymeric PBT salts

We measured absorption spectra of the polymeric IPCT complexes. Fig. 3 shows absorption spectra of  $\text{PBT}^{2+}2\text{Br}^-$  in various solvents. The well-defined absorption band around  $\lambda = 450 \text{ nm}$  was observed in addition to the absorption band of DPBT around  $\lambda = 380 \text{ nm}$ . The absorption band around  $\lambda = 380 \text{ nm}$  can be assigned to the LE band of the bithiophene moiety with  $\pi-\pi^*$  character. The pyridine rings at both sides of bithiophene possess electron accepting ability by the quaternization. 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  $\text{PBT}^{2+}2\text{I}^-$  in various solutions. The two absorption bands at  $\lambda = 385 \text{ nm}$  and shoulder at  $\lambda = 410 \text{ nm}$  were observed in all solutions, which is similar to the absorption character of  $\text{PBT}^{2+}2\text{Br}^-$ . The absorption spectra of  $\text{PBT}^{2+}2\text{Br}^-$  and  $\text{PBT}^{2+}2\text{I}^-$  in cyclohexane indicated absorption tailing up to  $\lambda = 700 \text{ nm}$ , 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  $\text{PBT}^{2+}2\text{Br}^-$  and  $\text{PBT}^{2+}2\text{I}^-$  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  $\text{PBT}^{2+}$ . The spectral shape of  $\text{PBT}^{2+}2\text{I}^-$  in DMF solution is unclear in comparison with other solutions.

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