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Synthesis and Physical Properties of Polyfluorene Derivative with Imidazolium Units

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A new polyfluorene derivative (PF-ImBr) with imidazole cations as side chains was synthesized to achieve a bidirectional photo-electro conversion by single-component polymer light-emitting electrochemical cell and photovoltaic cell with frozen p-i-n junction at room temperature. Various physical properties of this polymer such as UV-vis absorption and fluorescence spectra, transient absorption, fluorescence lifetime, and thermograms were studied. The optical band gap value of PF-ImBr was estimated as 2.9 eV. The transient absorption spectra and fluorescence lifetime results strongly suggested no electronic interactions between fluorene chromophores in the main chain and imidazolium cations in the side chain. PF-ImBr film with a fluorescent chromophore and two cations in the repeating units can form a single component frozen p-i-n junction after being heated above 130°C.

Keywords Ionic polyfluorene derivative; polymer frozen p-i-n junction; polymer light-emitting electrochemical cell; thermal properties; ultrafast dynamics

Introduction

Polymer frozen p-i-n junction can provide a novel approach to bidirectional photo/electro conversion. Polymer light-emitting electrochemical cells (PLEC) show light emission from electrochemical reactions [1]. To form frozen p-i-n junction in the PLEC, a ternary mixture of ions, a solid polymer electrolyte and conjugated polymer has been used as active materials in order to provide necessary ions, ion solvation and conducting moieties. The p-i-n junction in the PLEC device is formed as a result of electrochemical redox doping on the conjugated polymers and the associated redistribution of ions in the solid electrolyte above its glass transition temperature (T_g). Subsequently the p-i-n junction is stabilized by cooling it below T_g under applied constant bias voltage, this p-i-n junction is thus called 'frozen' p-i-n junction [2]. The p- and n-type doped regions provide ohmic contacts for balanced charge injection [3]. Light emission occurs in the insulating (i) region in between them. The PLEC with frozen p-i-n junction has advantages of light-emission at a lower driving voltage, corresponding to the band gap of the polymer and insensitivity to the choice of electrode materials and polymer thickness [4]. It is in contrast to

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conventional organic light-emitting diodes (OLED) which require a low work function cathode and a high work function anode sandwiching a very thin film of conjugated polymer [5]. The PLEC with frozen p-i-n junction also show photovoltaic characteristics. As in inorganic p-n junction devices, the built-in potential on PLEC with frozen p-i-n junction arises from the difference in electrochemical potentials of p-doped and n-doped regions of the active material. Therefore photovoltaic cell with frozen p-i-n junction can achieve higher open circuit voltage than that of other polymer-based photovoltaic cells which determine their built-in potentials by the workfunction difference of the electrodes [4,6].

As described above, a ternary mixture of ions, a solid polymer electrolyte and conjugated polymer has been used as active material to form frozen p-i-n junction in the PLEC. Because polymers with different charges are used, such systems often suffer from phase separation problem [7,8]. A single-component polymer photovoltaic cell with frozen p-i-n junction was recently proposed to solve such problems [9].

In this study new polyfluorene derivative (PF-ImBr) with imidazole cations as side chains was synthesized as one of most prominent candidates to form single-component PLEC and photovoltaic cell with frozen p-i-n junction at room temperature. Various physical properties of this polymer including transient absorption, fluorescence lifetime, and thermal behavior were studied.

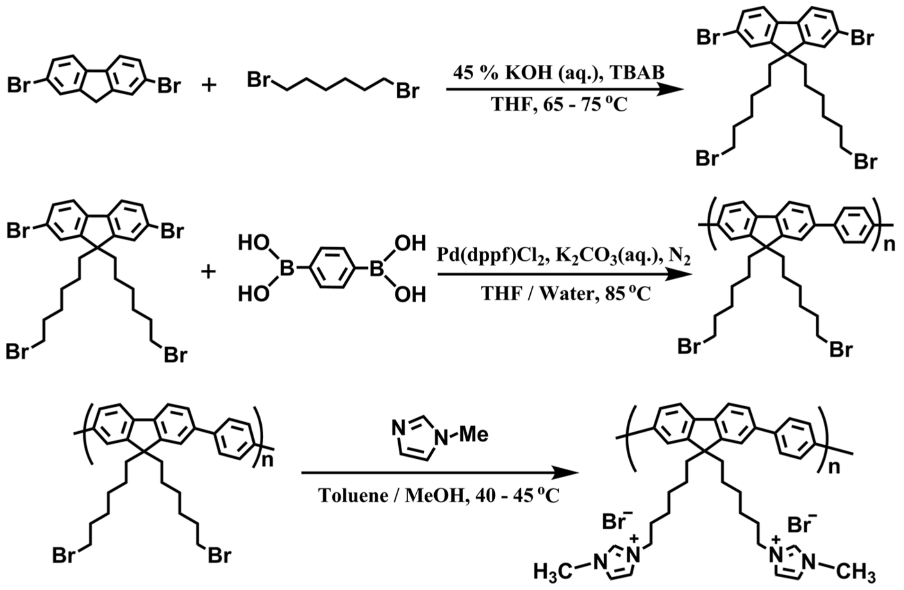
Experimental

Measurements. ^{1}H NMR and ^{13}C NMR spectra were recorded on a JNM-ECP 400. UV-visible absorption spectra and fluorescence spectra were obtained from Hitachi U-4100 spectrophotometer and Hitachi F-4500 fluorescence spectrophotometer. Thermal property was studied by differential scanning calorimetry (DSC) under a nitrogen atmosphere using a DSC 6220, (EXSTAR 6000, Seiko instrument).

Materials

The ionic polyfluorene derivative (PF-ImBr) with imidazolium bromide as side chains was synthesized by 'Suzuki coupling reaction' and subsequent reaction with N-methylimidazole [9,10]. Synthetic procedure for ionic polyfluorene derivative, PF-ImBr is shown in Scheme 1.

2,7-Dibromo-9,9-bis(6′-bromohexyl)fluorene:monomer. 2,7-dibromofluorene (6 g, 18.51 mmol, 1 Eq.) and tetrabutylammonium bromide (1.851 mmol, 0.1 Eq.) were dissolved in THF (40 ml) and 1,6-dibromohexane(14.90 g, 61.10 mmol, 3.3 Eq.) was added. Then 16 ml of 45% aqueous KOH aqueous solution was injected. The solution was stirred at 65–75°C for 5 h. The reaction mixture was poured into 300 ml of chloroform and neutralized by dilute hydrochloric acid. It was then extracted by water and chloroform several times. The organic layer was added by magnesium sulfate. The resulting solution was evaporated under vacuum. The reaction mixture was purified by column chromatography using hexane and chloroform (hexane:chloroform = 16:1) as an eluent. The product was a white solid with 45% yield. ^{1}H-NMR ($CDCl_3$, 400 MHz, TMS, δ) as shown in Figure 1: 7.52 (d, 2H, J = 8.0), 7.46 (dd, 2H, J = 1.8 and J = 8.0), 7.43 (d, 2H, J = 1.8), 3.29 (t, 4H, J = 6.7), 1.92 (m, 4H, J = 8.0), 1.67 (m, 4H, J = 7.3), 1.20 (m, 4H), 1.08 (m, 4H), 0.62-0.54 (m, 4H).



Scheme 1. The synthetic procedure of new ionic polyfluorene derivative with imidazolium bromide as side chains (PF-ImBr).

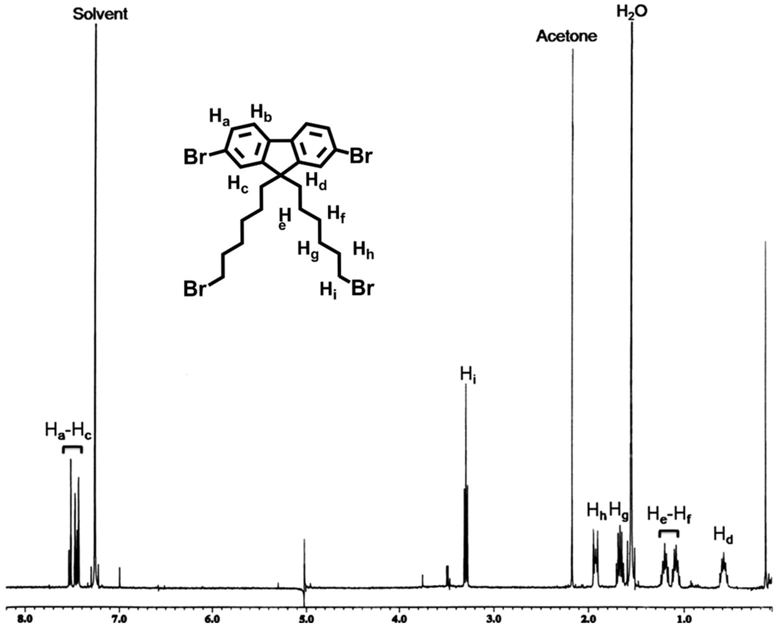


Figure 1. ^{1}H-NMR spectrum of 2,7-Dibromo-9,9-bis(6′-bromohexyl)fluorene as a mononor in chloroform-d.

Poly[9,9-bis(6′-bromohexyl)fluorene-co-alt-1,4-phenylene] (PF-Br):neutral polymer. 2,7-Dibromo-9,9-bis(6′-bromohexyl)fluorene (1.961 g, 3.0 mmol, 1 Eq.), 1,4-phenyldiboronic acid (0.504 g, 3.0 mmol, 1 Eq.), Pd(dppf)Cl_2 (46 mg), potassium carbonate (4.2 g, 30.0 mmol, 10 Eq.), and a small amount of tetrabutylammonium-bromide (40 mg) in a 50 ml round bottom flask. After adding a mixture of water (15 ml) and tetrahydrofuran (20 ml), the solution was degassed. The mixture was refluxed at 85°C for 30 h under nitrogen. After adding phenylboronic acid (0.121 g, 1 mmol) the solution was further refluxed for another 3 h, followed by the addition of bromobenzene (0.156 g, 1 mmol). This process helps to increase the degree of polymerization by reacting terminal moieties (residual brome and boronic acid) of polymer chains. The mixture was refluxed for another 1 h and then cooled down to room temperature. It was poured into a mixture of methanol (300 ml) and water (30 ml). The precipitate was filtered and washed with methanol. The precipitate was dissolved in chloroform and washed with chloroform. After removing the chloroform, the solid was re-precipitated with methanol. The solid was dissolved in acetone and was filtered and washed with acetone. A neutral polymer was obtained as a yellow solid in 54% yield. ^{1}H-NMR ($CDCl_3$, 400 MHz, TMS, δ) as shown in Figure 2: 7.8 (m, 5H), 7.7-7.6 (m, 4H), 7.5 (m, 1H), 3.3 (t, 4H), 2.1 (m, 4H), 1.7-1.6 (m, 4H), 1.2-1.1 (m, 8H), 0.7 (m, 4H), ^{13}C-NMR ($CDCl_3$, 400 MHz, TMS, δ): 151.9, 140.9, 140.6, 140.1, 128.0, 126.6, 121.8, 120.6, 55.6, 40.8, 34.4, 33.1, 29.5, 28.2, 24.1, Gel permeation chromatography in THF (polystyrene standard): M_n: 33,000 g/mol, M_w: 93,000 g/mol, and PDI = 3.0.

Poly(9,9-bis[6′-(3″-methyl-1″-imidazolium)hexyl]fluorene-co-alt-1,4-phenylene) dibromide (PF-ImBr):ionic polymer. 0.1 g of poly[9,9,-bis(6′-bromohexyl)fluorene-co-alt-1,4-phenylene] and 3.11 g of N-methylimidazole were dissolved in 16 ml of toluene. The mixture was refluxed at 43–44°C for 2.5 h under nitrogen. A solid

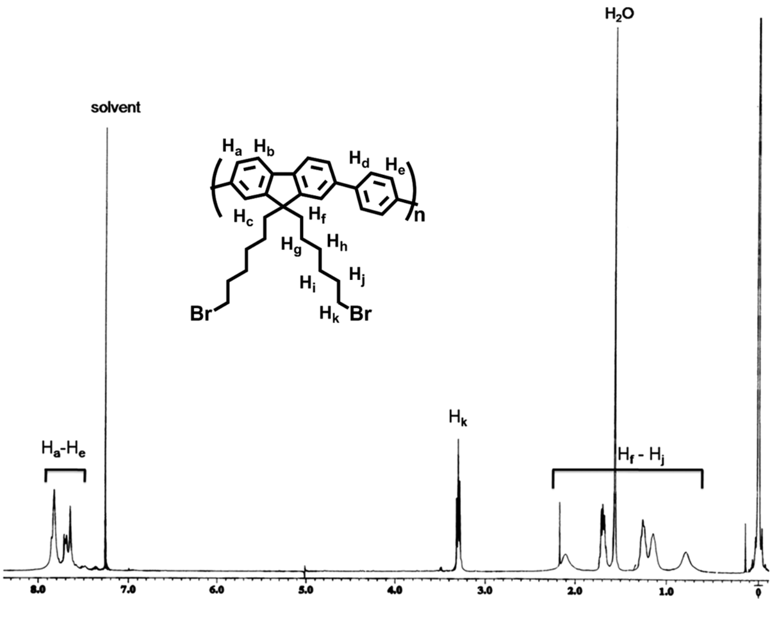
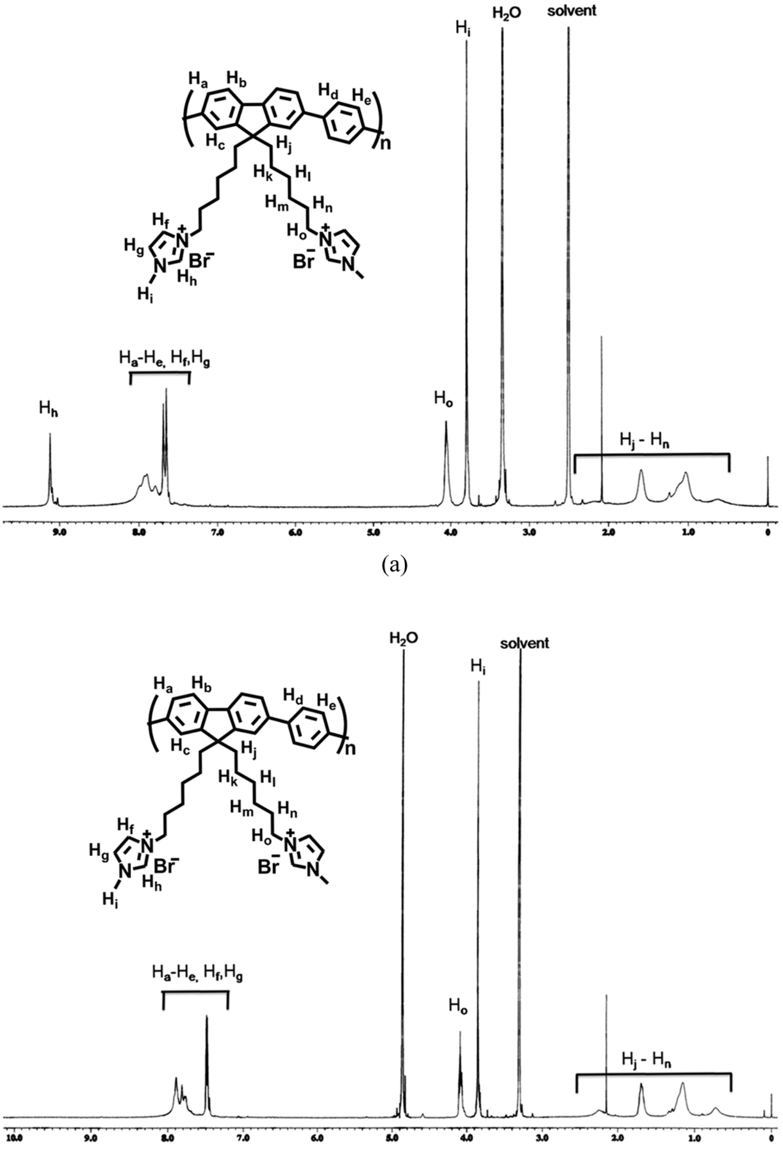


Figure 2. ^{1}H-NMR spectrum of PF-Br as a neutral polyfluorene derivative in chloroform-d.

was precipitated in toluene. Then 20 ml of methanol was added to the reaction mixture to dissolve the solid. The reaction mixture was refluxed for 43 h. The mixture was cooled to room temperature. The mixture was filtered to remove solid impurities generated by side reaction. The filtered solution was evaporated under vacuum to remove the solvents at 40°C. Brown liquid which contained excess of N-methylimidazole was obtained. 20 ml of acetone was poured to the liquid to reprecipitate. Yellow solid was filtered under vacuum and washed by acetone.



(a)

(b)

Figure 3. (a) ^{1}H-NMR spectra of PF-ImBr as an ionic polyfluorene derivative in dimethylsulfoxide-d$_6$; (b) ^{1}H-NMR spectra of PF-ImBr as an ionic polyfluorene derivative in methanol-d$_4$.

0.123 g of yellow solid was obtained as the purpose polymer with NMR spectra shown in Figure 3. ^{1}H-NMR (CD_3SOCD_3, 400 MHz, TMS, δ): 9.09 (s, 2H), 8.46-7.74 (br, 8H), 7.74-7.53 (d, 5H), 4.15-3.94 (br, 4H), 3.90–3.71 (br, 6H), 2.31-1.95 (br, 1H), 1.84-1.46 (br, 4H), 1.36-0.79 (br, 8H), 0.79-0.21 (br, 2H), ^{1}H-NMR (CD_3OD, 400 MHz, TMS, δ): 8.29-7.63 (m, 9H), 7.63-7.3 (d, 5H), 4.24-4.0 (t, 4H),3.85 (s, 6H), 2.52-1.92 (br, 2H), 1.94-1.46 (br, 4H), 1.46-0.96 (br, 8H), 0.96-0.32 (br, 3H).

Characterization

Films for UV-visible absorption and fluorescence spectra were prepared by casting 0.5 wt % solution of PF-ImBr in methanol and then drying in vacuum for 56 h at room temperature. All measurements were performed at room temperature. PF-ImBr films for transient absorption and time resolved fluorescence measurements were prepared according to the same method. Transient absorption spectra were measured by a pump-probe method with femtosecond (fs) white light in the visible region as a probe, with fs pump of 23 μJ/pulse at 400 nm. Figure 4 shows a schematic diagram of the pump-probe fs transient absorption measurement system. Fluorescence decays were measured by the single-photon counting method using a streak scope. The PF-ImBr film was excited with SHG ($\lambda = 390$ nm) of a mode-looked Ti:sapphire laser. Differential scanning calorimetry (DSC) was performed under nitrogen for two samples of PF-ImBr powder sealed in Al pans. After the first heating scan, the recorded DSC thermograms provide essentially the same thermal behavior at heating rate 10°C/min from −100°C to 260°C. One sample (a) was rapidly cooled to −100°C at 20°C/

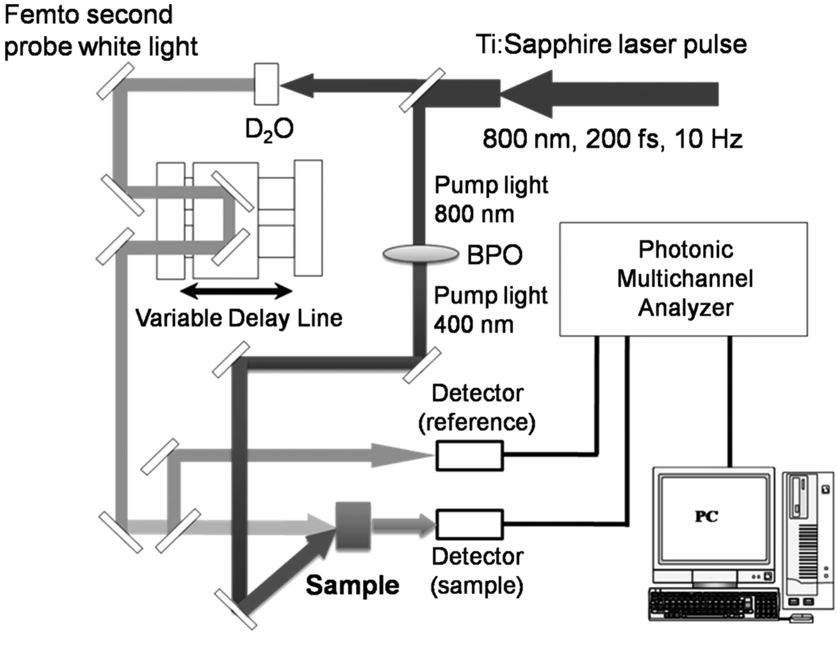


Figure 4. Schematic diagram of the pump-probe femtosecond transient absorption measurement system.

min after keeping at 260°C for 20 min. Another sample (b) was slowly cooled to −100°C from 260°C at 0.5°C/min.

Results and Discussion

As shown in Scheme 1, the monomer was easily prepared from 2,7-dibromofluorene. The neutral polymer (PF-Br) was synthesized by 'Suzuki coupling reaction' with diboronic acid and the ionic polymer (PF-ImBr) was achieved via quaternization of the neutral polymer with N-methylimidazole in a toluene/methanol mixture. Figures 1–3 show the ^{1}H-NMR spectra of the monomer, the neutral polymer and the ionic polymer, respectively. The NMR spectra indicate that the polyfluorene derivatives were obtained clearly. In the Figure 3, ^{1}H-NMR analysis of the ionic polymer (PF-ImBr) was performed by two solvents of dimethylsulfoxide-d_6 and methanol-d_4 to analyze more clearly. They corresponded well with expected structure.

Figure 5 shows the UV-visible absorption and fluorescence spectra of PF-ImBr films. The absorption onset and absorption maximum of PF-ImBr film appeared at 430 nm and 383 nm, respectively. The optical band gap value ($E_{\mathrm{opt}} = 1240/\lambda_{\mathrm{onset}}$ eV) of PF-ImBr was estimated as 2.9 eV from the onset wavelength. It will give the driving voltage for the PLEC or the build-in potential in the photovoltaic cell with frozen p-i-n junction using this ionic polymer. In fluorescence spectra, the emission peaks of PF-ImBr film appeared at 433 nm and 450 nm corresponding to blue emission.

Transient absorption spectra and fluorescence lifetime were measured to investigate excited state dynamics and any possible interactions between polyfluorene main chain and imidazole cations in the side chain. Figure 6 shows transient absorptions in the visible region. Two transient absorption peaks were observed at 600 nm and 730 nm. The transient absorption spectra for PF-ImBr can be compared with the previous study for a poly(9,9-dioctylfluorene) (PFO) film [11]. The transient absorption spectrum of PFO film was reported to show the absorption bands at 600 nm and 750 nm in the visible region [11]. The absorption bands with peaks at 600 nm and 750 nm were assigned to the photoinduced absorption by polarons and excitons, respectively from the much slower decay of transient absorptions at 600 nm than that at 750 nm under same pump power [11]. Almost similar transient absorption spectra

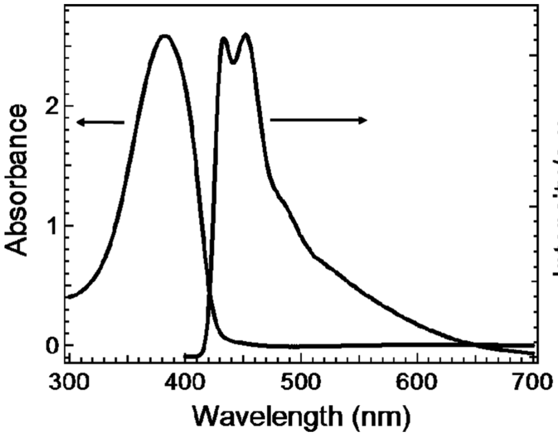


Figure 5. UV-visible absorption and fluorescence spectra of PF-ImBr films.

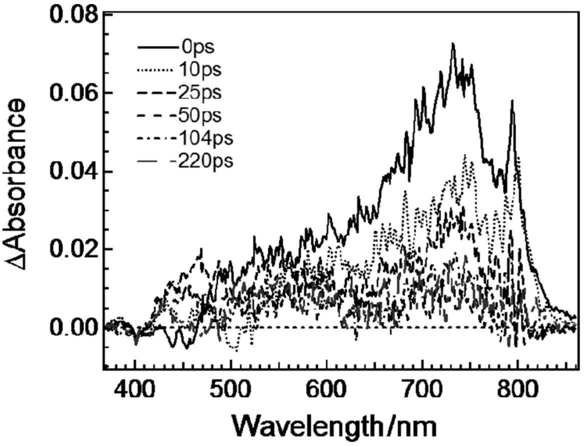
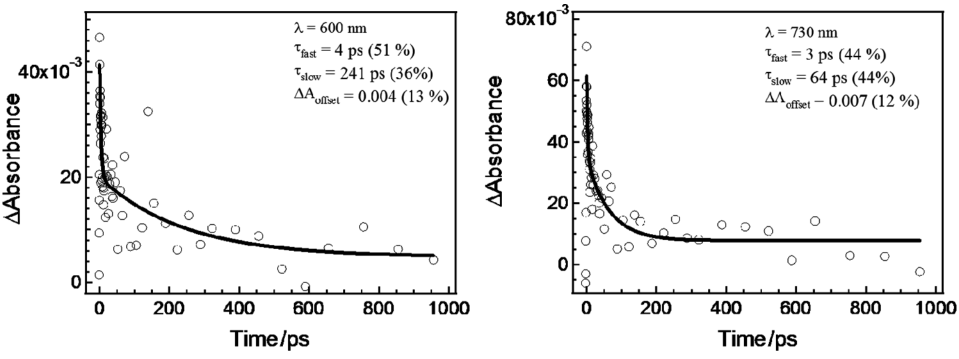


Figure 6. Transient absorption spectra of PF-ImBr film upon excitation with fs laser at 400 nm (23 μJ/pulse).

were observed in the present polymer, PF-ImBr as shown in Figure 6. A time profiles of transient absorption at 600 nm and 730 nm of the PF-ImBr film are shown in Figure 7(a) and (b), respectively. The time profiles can be analyzed by the following equation, $\Delta A = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) + A_{\text{offset}}$, where A and τ denote initial absorbance and lifetime of each component, respectively. The subscripts 1 and 2 correspond to fast and slow decaying excited states of PF-ImBr and the offset means a component which does not decay in the time region studied. The time profile of transient absorption at 600 nm was fitted by this equation with time constants and relative contributions of 4 ps (51%), 241 ps (36%) and an offset (13%) (Fig. 7 (a)). Meanwhile, the time profile of transient absorption at 730 nm was fitted by the similar equation with components of 3 ps (44%), 64 ps (44%) and an offset (12%) (Fig. 7 (b)). In these time profiles, it is observed that the time decays of the transient absorption band at 600 nm are slower than those of the absorption band at 730 nm. From these results, the absorption bands at 600 nm and at 730 nm can be corresponded to photoinduced



(a) (b)

Figure 7. (a) Time profile of transient absorption at 600 nm for PF-ImBr film upon excitation with fs laser at 400 nm (23 μJ/pulse); (b) Time profile of transient absorption at 730 nm for PF-ImBr film upon excitation with fs laser at 400 nm (23 μJ/pulse).

absorptions by polarons and excitons, respectively. The fluorescence decay for PF-ImBr film was found to be almost single exponential with a lifetime of $\tau = 50$ ps (96%). This value corresponded well with the slow decay constant ($\tau_2 = 64$ ps) in transient absorption at 730 nm. This is another supporting evidence that the transient absorption at 730 nm was due to the absorption from the first S_1 to the higher excited singlet state (S_n) of polyfluorene unit. The observed fast component ($\tau_1 = 3$ ps) is most probably attributed to S_1-S_1 annhilation due to increased local concentration of excited singlet states in solid polymer films. No electronic interaction is likely to occur between the main chain of polyfluorene and imidazole cations from these results.

Thermal behavior of PF-ImBr was studied in DSC thermograms. The quenched sample (a) showed an exothermic peak at 25°C and an endothermic peak at 90°C. The slowly cooled sample (b) showed two exothermic peaks and two endothermic peaks. Two exothermic peaks appeared at 27°C and at 43°C, respectively and two endothermic peaks appeared at 85°C and 128°C, respectively. Crystallization and melting of side chains of PF-ImBr and main chains of polyfluorene most probably contributed to each peaks. From these results, the frozen p-i-n junction for PLEC at room temperature using PF-ImBr film can be formed after heating above 130°C to help the ions migrate freely in the film under applied bias. Transparent yellow cast films were obtained at room temperature, which strongly suggests the crystalline domains of this polymer were smaller than about 1 μm.

Conclusions

PF-ImBr was synthesized as a candidate to form frozen p-i-n junction for PLEC at room temperature. Fundamental physical properties of this polymer were studied to elucidate excited dynamics and thermal stability. The optical band gap value of PF-ImBr was estimated as 2.9 eV. The transient absorption spectra and fluorescence lifetime results strongly suggested no electronic interactions between fluorene chromophores in the main chain and imidazolium cations in the side chain. PF-ImBr film with a fluorescent chromophore and two cations in the repeating units can form a single component frozen p-i-n junction after being heated above 130°C.

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