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Phosphorescent chelating polyelectrolytes and their neutral precursors: Synthesis, characterizations, photoluminescence and electroluminescence

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Abstract

Novel chelating polyfluorene polyelectrolytes and their corresponding neutral precursors with Ir complex incorporated into polymer backbone were synthesized by Suzuki polycondensation reaction. The aminoalkyl or quaternized ammonium group provides good solubility of these phosphorescent polymers in alcohols which has a great advantage in fabrication of multi-layer polymer phosphorescent PLEDs. The photophysical and electroluminescent properties of the phosphorescent polyelectrolytes and their neutral precursors were investigated. The phosphorescent emission bands from both polyelectrolytes and neutral polymers which lie at around 640 nm displayed a saturated red emission. Devices fabricated from these phosphorescent polymers with air-stable high work function metals, such as Al, as cathode showed comparable device performance with low work function metals, such as Ba.

Keywords: Chelating polyelectrolytes; Iridium complex; Electroluminescence

1. Introduction

Conjugated polymers have attracted much attention because of their solution processability, mechanical flexibility, color tunability and low operating voltage [1–3]. Commonly, conjugated polymers are electrofluorescent and only singlet emission is utilized in polymer light-emitting devices (PLEDs) [1–5]. Therefore, it is necessary to focus on utilizing both singlet and triplet emission in PLEDs for improving the electroluminescent efficiencies. Up to now, many works have been devoted to the field. For example, Jiang et al. [6] and Yang et al. [7] have utilized the blended systems between the polymer host and small molecular Ir complex guest to achieve highly efficient PLEDs. Another important way to realize both singlet and triplet emission is to attach phosphorescent metal complex to the polymer side and/or main chain, which can reduce the aggregation of the phosphor, triplet–triplet quenching and phase separation [8]. For instance, Chen et al. [9] first reported conjugated polymers containing Ir complex at the polymer side chains and showed comparable device performance with that of blended systems. Jiang et al. [10,11] developed a series of fluorene-*alt*-carbazole polymers with different Ir complexes at the polymer side chain and achieved a good device performance. Evans et al. [12] researched the triplet back transfer between the polymer backbone and the Ir complex by changing the side chain length. More recently, Sandee et al. [8] and Zhen et al. [13,14] developed a different synthetic strategy to covalently incorporate Ir complex into a conjugated polymer main chain. The conjugated polymers synthesized by Zhen et al. [14] have an external quantum efficiency of 6.5% photon/electron (ph/el) at the current density of 38 mA/cm^2. The efficiency remains as high as 5.3% ph/el at a high current density of 100 mA/cm^2 showing no remarkable efficiency decay at high current density.

Recently, conjugated polyelectrolytes (CPs), which often have the ionic side groups attached to the main chain of

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conjugated polymers, have attracted great interest due to their possible applications in the biological and chemical sensors [15], self-assembly systems [16] and electroluminescent devices [17–19]. Compared to the success in the biological field [20,21], the CPs were not ideal materials as light-emitting layer in polymer light-emitting diodes (PLEDs) and the device performances reported so far were very poor. However, more recently reports by our group showed that the device performances from conjugated polyelectrolyte can be greatly improved by incorporating some narrow band gap comonomers into polymer main chain and the emission color can be tuned from green to red [22–25,28]. More importantly, the polymers can provide good device performances by using high work function metal, such as Al, Ag and Au, as cathode [26–28]. Most recently, we reported a series of conjugated polyelectrolytes and their neutral precursor with a neutral Ir complex $Ir(ppy)_3$ (up to 10%) incorporated *via* 3,8-phenylpyridine into aminoalkyl-substituted (or quaternized) polyfluorene backbone as a ligand and efficient orange-phosphorescent PLEDs were achieved with high work function metals, such as Al, Au as cathodes [29].

In this paper, we report a series of novel chelating phosphorescent polyelectrolytes and their neutral precursor with Ir complex incorporated into aminoalkyl-substituted polyfluorene main chain with ionic group in the polymer side chain. In contrast to our previous work, two bromine atoms in different ligands (naphthinatopyridine) of iridium acetylacetonate complex were used as a comonomer in the Suzuki coupling with fluorenes resulting in chelating copolymers with Ir atoms on the polymer backbone. The synthesis and characterization of these new type of phosphorescent polyelectrolytes and their neutral precursors are described and the photophysical and electroluminescent properties are also investigated.

2. Experimental part

2.1. Materials

All reagents, unless otherwise specified, were obtained from Aldrich, Acros and used as received. Compounds 5-bromo-2-(4-methyl-1-naphthalene)pyridine (**1**) [30], 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (**4**) [31] and 2,7-dibromo-9,9-bis(3′-(*N*,*N*-dimethylamino)propyl)fluorene (**5**) [22] were prepared following the published procedures.

2.2. General methods

^{1}H NMR spectra were recorded on a Bruker DRX 300 spectrometer operating at 300 MHz. Analytical GPC was obtained using a Waters GPC 2410 in tetrahydrofuran (THF) *via* a calibration curve of polystyrene standards. Elemental analysis was performed on a Vario EL Elemental Analysis Instrument (Elementar Co.). UV–vis absorption spectra were measured on a HP 8453 spectrophotometer. PL spectra in solutions were taken by Fluorolog-3 spectrofluorometer under 380 nm light excitation.

2.3. Device fabrication and measurement

LED was fabricated on pre-patterned indium–tin oxide (ITO) with a sheet resistance of 10–20 Ω/□. Onto the ITO glass a layer of polyethylenedioxythiophene–polystyrene sulfonic acid (PEDOT:PSS) film with a thickness of 50 nm was spin-coated from its aqueous dispersion (Baytron P 4083, Bayer AG), aiming at improving the hole injection and avoiding the possibility of leakage. Then, a thickness of 40 nm of PVK layer was spin-coated to improve the hole transport. The solution of the copolymers in toluene (for neutral) or methanol (for polyelectrolytes) was prepared in a nitrogen-filled dry box and spin-coated on the top of the ITO/PEDOT:PSS surface. The typical thickness of the emitting layer was 70–80 nm. Then a thin layer of barium (Ba) as an electron injection cathode and/or the subsequent 200 nm thick aluminum capping layers were thermally deposited by vacuum evaporation through a mask at a base pressure below 2×10^{-4} Pa. Current–luminance–voltage (*I*–*L*–*V*) characteristics were measured with a computerized Keithley 236 Source Measure Unit and calibrated Si photodiode. EL spectra were taken by InstaSpec™ IV CCD spectrograph.

2.4. Synthesis

2.4.1. Iridium(III) bis(5-bromo-2-(4-methyl-1-naphthalene)pyridine-C^2,N) acetylacetate (3)

Iridium(III) trichloridehydrate (6.47 g, 18.3 mmol), 5-bromo-2-(1-naphthalene) pyridine (2.1 g, 7.34 mmol), 2-ethoxyethanol (30 mL) and water (10 mL) were added into a two-necked flask. The mixture was refluxed under an argon atmosphere for 20 h and then cooled to room temperature. A red precipitate was filtered and washed with water and ethanol several times. The resulting red solid was purified by column chromatography. Then the dried product (358 mg, 0.22 mmol) was mixed with acetylacetone (55 mg, 0.55 mmol) and sodium carbonate (70 mg) in degassed 2-ethoxyethanol (15 mL) in a two-necked flask. The mixture was refluxed in an argon atmosphere for 10 h. After cooling to room temperature the red precipitate was formed. After being filtered and washed with water and ethanol, the precipitate was purified by column chromatography to get the red crystal product, 310 mg (yield: 81%). ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 8.60 (d, $J = 2.16$ Hz, 2H), 8.47 (d, $J = 8.52$ Hz, 2H), 8.38 (d, $J = 9.03$ Hz, 2H), 7.94 (d, $J = 2.28$ Hz, 2H), 7.92 (d, $J = 2.28$ Hz, 2H), 7.82 (d, $J = 8.25$ Hz, 2H), 7.50 (t, $J = 8.31$, 1.17 Hz, 2H), 7.33 (t, $J = 7.14$ Hz, 2H), 6.14 (s, 2H), 5.32 (s, 1H), 2.35 (s, 6H), 1.86 (s, 6H). Calcd. for $C_{37}H_{31}N_2O_2Br_2Ir$: C, 50.06; H, 3.52; N, 3.16. Found: C, 50.32; H, 3.44; N, 3.18.

2.5. Synthesis of polymer

The comonomer feed ratios of **5** to **3** are 99:1, 98:2, 96:4, 90:10 and 84:16 and always keep $\mathbf{5} + \mathbf{3} = \mathbf{4}$ mol, and the molar ratio of complex **3** in polymers is 0.5, 1, 2, 5 and 8%, the corresponding polymers were named PFN–MeNaPyIr05, PFN−MeNaPyIr1, PFN−MeNaPyIr2, PFN−MeNaPyIr5 and PFN−MeNaPyIr8, respectively.

The preparation of polymer PFN−MeNaPyIr1 is given as a typical example. 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (**4**) (642 mg, 1.00 mmol), 2,7-dibromo-9,9-bis(3′-(*N*,*N*-dimethylamino)propyl)fluorene (**5**) (489 mg, 0.99 mmol), **3** (8.86 mg, 0.01 mmol), $Pd(OAc)_2$ (7 mg) and PCy_3 (15 mg) were dissolved in a mixture of 10 mL toluene and 4 mL of Et_4NOH aqueous solution. The mixture was refluxed with vigorous stirring for 2 days under argon atmosphere. A small amount of **1** was added and after 12 h 0.5 mL of bromobenzene was added. Then the mixture was cooled to room temperature, and the solution was filtered and the filtrate was poured into methanol. The precipitated material was recovered by filtration through a funnel. The resulting solid material was washed for 24 h using acetone to remove oligomers and catalyst residues (0.52 g, 80%). ^1H NMR (300 MHz, $CDCl_3$, δ ppm): 7.87−7.84, 7.73−7.63, 7.54−7.49, 7.38−7.36, 6.93, 2.08, 1.70, 1.31, 1.28, 1.50, 1.00, 0.85−0.81. Elemental Anal. Found: C, 83.47; H, 9.01; N, 3.54. Molecular weight: $M_n = 12{,}100$, PDI = 1.40.

PFN−MeNaPyIr05: ^1H NMR (300 MHz, $CDCl_3$, δ ppm): 7.87−7.84, 7.73−7.67, 2.12−2.05, 1.75, 1.42, 1.15, 0.98, 0.85−0.81. Elemental Anal. Found: C, 84.52; H, 9.17; N, 3.70. Molecular weight: $M_n = 25{,}100$, PDI = 2.10.

PFN−MeNaPyIr2: ^1H NMR (300 MHz, $CDCl_3$, δ ppm): 7.87−7.84, 7.73−7.63, 7.56−7.51, 7.38−7.34, 6.93, 2.08, 1.66, 1.28, 1.15, 0.99, 0.86−0.81. Elemental Anal. Found: C, 82.57; H, 8.89; N, 3.43. Molecular weight: $M_n = 21{,}850$, PDI = 2.10.

PFN−MeNaPyIr5: ^1H NMR (300 MHz, $CDCl_3$, δ ppm): 7.84, 7.74−7.63, 7.55−7.51, 7.38−7.35, 6.93, 2.09, 1.62, 1.43, 1.35, 1.27, 0.83. Elemental Anal. Found: C, 82.43; H, 9.04; N, 3.45. Molecular weight: $M_n = 15{,}800$, PDI = 2.00.

2.6. General procedure for preparation of quaternization polymers PFNBr−MeNaPyIr

The preparation of polymer PFNBr−MeNaPyIr1 is given as a typical example.

A 100 mL flask with a magnetic stirring bar was charged with PFN−MeNaPyIr1 (110 mg) dissolved in 40 mL of THF. To the polymer solution was added excess bromoethane and 10 mL of DMSO. The solution was stirred at 50 °C for 5 days. THF and extra bromoethane were evaporated. The quaternized polymer was precipitated in about 100 mL ethyl acetate, collected by centrifugation and washed with acetone, THF and dried overnight in vacuum at 80 °C. Yield: 68%. ^1H NMR (300 MHz, DMSO-d_6, δ ppm): 9.26, 8.07−7.89, 3.94, 2.83−2.81, 2.58−2.57, 2.52−2.51, 2.34, 1.07, 0.79−0.75.

PFNBr−MeNaPyIr05: ^1H NMR (300 MHz, DMSO-d_6, δ ppm): 9.24, 8.06−7.70, 4.09, 2.83, 2.57−2.55, 2.52−2.51, 2.35, 1.36, 1.12−1.07, 0.79−0.75.

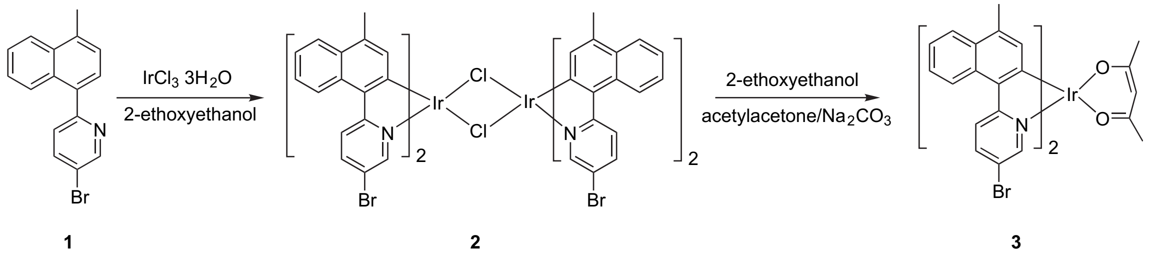
PFNBr−MeNaPyIr5: ^1H NMR (300 MHz, DMSO-d_6, δ ppm): 9.27, 8.07−7.90, 4.06, 2.84−2.81, 2.57−2.54, 2.52−2.51, 2.35, 1.07, 0.79−0.75.

3. Results and discussion

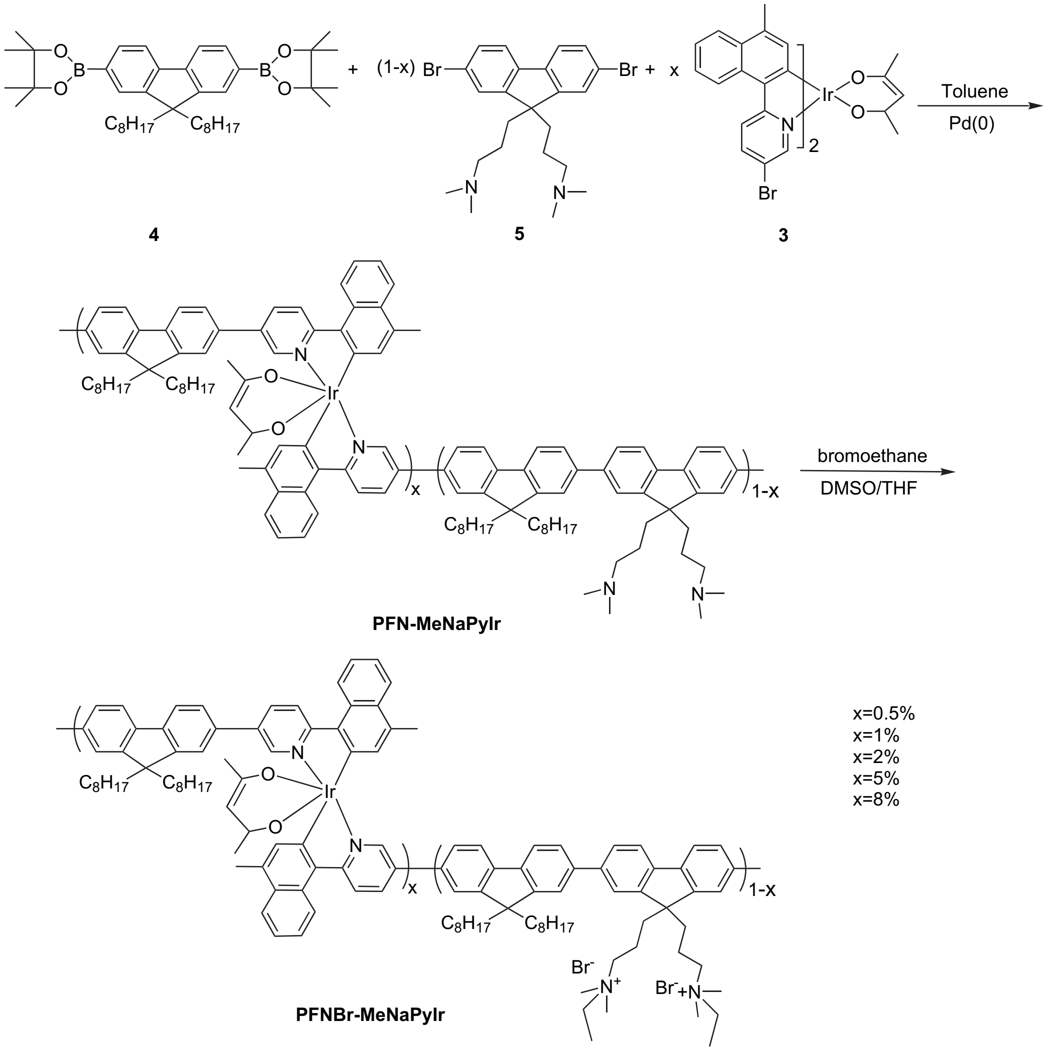
3.1. Synthesis and characterization

Compounds **1** [30], **4** [31] and **5** [22] were synthesized according to the literature procedures. Scheme 1 illustrates the synthetic route of compound **3**. Firstly, $IrCl_3 \cdot 3H_2O$ and **1** reacted in 2-ethoxyethanol/H_2O (3:1) to give the bridged dimer **2** in good yield [32]. The reaction between the dimer **2** and acetylacetonate provided compound **3** following careful purification by column chromatography in 81% yield. The results from ^1H NMR and elemental analysis gave the evidence that complex **3** had the desired structure and high purity. The neutral polymers were prepared by the Pd-catalyzed Suzuki polymerization under slightly modified conditions as shown in Scheme 2. All these resulting polymers are soluble in common organic solvents such as $CHCl_3$, toluene and THF. Importantly, these neutral polymers are also soluble in CH_3OH by adding several drops of weak acid, such as acetic acid, which is due to the weak interaction formed between the nitrogen atoms and the acetic acid [22−25,28,29]. The chemical structures of these polymers were characterized by ^1H NMR and elemental analysis. The molecular weights of these polymers were determined by gel permeation chromatography (GPC) with polystyrene as reference. The number-average molecular weight (M_n) of these polymers is between 12,000 and 25,000 with polydispersity index (PDI) of 1.40−2.10.

The neutral polymers were quaternized with bromoethane in DMSO/THF (1:4) for 5 days to provide the corresponding polyelectrolytes. Three neutral polymers were quaternized and the obtained polyelectrolytes were named as PFNBr−MeNaPyIr05, PFNBr−MeNaPyIr1 and PFNBr−MeNaPyIr5, respectively. After quaternization, the solubility of these



Scheme 1. The synthetic route of monomer **3**.



Scheme 2. The synthetic routes of the copolymers.

polyelectrolytes is very different from that of netural polymers. The polyelectrolytes are completely soluble in polar solvents such as CH_3OH, DMF and DMSO and are insoluble in common organic solvents. The molecular weights of these polyelectrolytes are of the same order with that of corresponding neutral polymers due to the mild reaction condition of the quaternization [22].

The thermal stability of these polymers is investigated by thermogravimetric analysis (TGA). For neutral polymers (Fig. 1), the onset of degradation temperature (T_d) (5% mass loss) is around 390 °C. In contrast, the polyelectrolytes showed a more complicated degradation process compared to that of neutral polymers. For polyelectrolytes (Fig. 1), a slight weight loss at around 100 °C was observed, which is due to the small amount of water in polyelectrolytes. Another two degradation processes were found at around 190 and 400 °C, the former is attributed to the decomposition of the ionic side chain and the latter corresponds to the polymer main chain. These results indicate that the neutral and quaternized polymers have good thermal stability.

3.2. Absorption and photoluminescent properties

The absorption and emission spectral data of the neutral and quaternized polymers are summarized in Table 1. The UV–vis absorption and emission spectra of the neutral polymers in $CHCl_3$ and thin film state are shown in Figs. 2a and 3a. The absorption bands are almost identical with polyfluorene copolymers [31,33] for all neutral polymers with the absorption bands peaked at 387, 382 nm in solution and thin film, respectively. The absorption band is attributed to the $\pi-\pi^*$ absorption of the PFN segment [22,28,29]. It shows that incorporation of Ir complexes into the polymer main chain results in a very little change in the solution and solid state absorption spectra. No ^{3}MLCT absorption band from Ir complex in solution was observed due to the low iridium complexes content, which is similar to that observed in literature [13,14]. As shown in Fig. 2a, the emission spectra of the neutral polymers at around 0.02 g/L in $CHCl_3$ solution contains two features: one around 420 nm, which is dominant and assigned to the PFN emission; another very weak peak

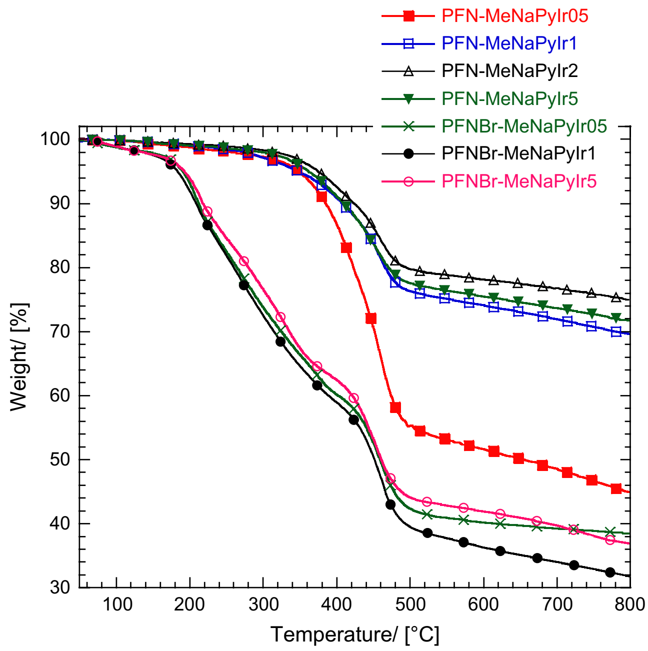


Fig. 1. Thermogravimetric analysis of neutral polymers and quaternized polymers in nitrogen atmosphere.

around 638 nm is attributed to the phosphorescent emission of Ir complex, intensity of which increases as the Ir complex content increased. This indicates that incorporation of iridium complexes into the PFN chain resulted in little change in the photoluminescent spectra in solution. However, there are significant changes in emission spectra in solid state compared to that in solution. As shown in Fig. 3a, the spectra were dominated by the emission at around 644 nm while a weak residue of blue emission at around 440 nm from the PFN segment was obtained, intensity of which decreases with increasing Ir complex content. As reported, the triplet energy of polyfluorene is 2.10 eV [34] and the triplet energy of the phosphor in PFN–MeNaPyIr, which was estimated from the phosphorescent emission wavelength, is 1.93 eV. Therefore, triplet energy transfer from the triplet state of PFN segment to that of Ir complex is exothermic and back transfer from triplet state of Ir complex to that of PFN segment is not favorable.

Figs. 2b,c and 3b show the UV–vis absorption and emission spectra of the quaternized polymers in methanol and DMSO solutions and in thin film. Unlike neutral polymers like PFN–MeNaPyIr, the electronic properties of PFNBr–MeNaPyIr depend on the solvent and absorption band shows a red-shift with an increase in solvent polarity. The dominated absorption peak in the absorption spectra of PFNBr–MeNaPyIr copolymers is similar and lies around 389 and 400 nm in methanol and DMSO, respectively, which is assigned to π–π* transitions of the PFNBr segment. The corresponding PL spectrum is also similar and PL peaks are observed at 417 and 424 nm with the vibronic shoulder around 438 and 447 nm, respectively, in methanol and DMSO. It is interesting to note that the PL spectra of polyelectrolyte up to 5% of Ir complex loading only show exclusively the blue emission responsible for PFNBr emission and no emission from iridium complex was detected. This may be attributed to the fact that after ionization, the polymer chains become twisted and intra-/inter-chain interaction is significantly reduced due to chain non-planarity. The UV–vis absorption and PL spectra of PFNBr–MeNaPyIr in film are shown in Fig. 3b and the absorption peak lies around 388 nm corresponding to the π–π* transitions of the PFNBr segment in thin film. Interestingly, the PL spectra of PFNBr–MeNaPyIr in thin film also shows only blue emission from PFNBr segments and no phosphorescent emission from Ir complex was found. This fact is a bit unusual and indicates that at low Ir complex loading (up to 5%), inter-chain interaction does not contribute to energy transfer from PFN to Ir complex in thin film. We note also the fact that for all polyelectrolytes, broad shoulder centered at around 530 nm can be observed for PL emission. The intensity of this feature is decreased with increasing Ir complex content. Similar feature was also observed for PFN homopolymer (without Ir complex incorporated) as reported previously by Huang et al. [22]. This feature was assigned to excimer emission of PFN segment [22] or in PFO homopolymer [35]. We note that for neutral copolymer PFN–MeNaPyIr05 the increased PL intensity in this region was observed too. However, for copolymer with higher Ir complex content, this excimer emission is completely depressed. This indicates that energy transfer from PFN to Ir complex

Table 1
The photophysical properties of these polymers in solution and thin film

Polymer	Solution		Film	
	Absorption λ_{max} (nm)	Emission λ (nm)	Absorption λ_{max} (nm)	Emission λ (nm)
PFN	389	419, 441	390	425, 449
PFN–MeNaPyIr05	388	423, 441	382	640 (453)[b]
PFN–MeNaPyIr1	386	421, 441	382	640 (452)[b]
PFN–MeNaPyIr2	387	420, 441	382	644 (456)[b]
PFN–MeNaPyIr5	388	421, 440, 636	383	644 (456)[b]
PFN–MeNaPyIr8	387	422, 442, 634	–	–
PFNBr	388 (400)[a]	416, 437 (424, 449)[a]	400	431, 455
PFNBr–MeNaPyIr05	389 (394)[a]	418, 438 (424, 447)[a]	388	426
PFNBr–MeNaPyIr1	389 (399)[a]	417, 437 (424, 447)[a]	388	427
PFNBr–MeNaPyIr5	389 (400)[a]	417, 438 (424, 447)[a]	390	427

[a] In DMSO solution.

[b] A weak emission shoulder.

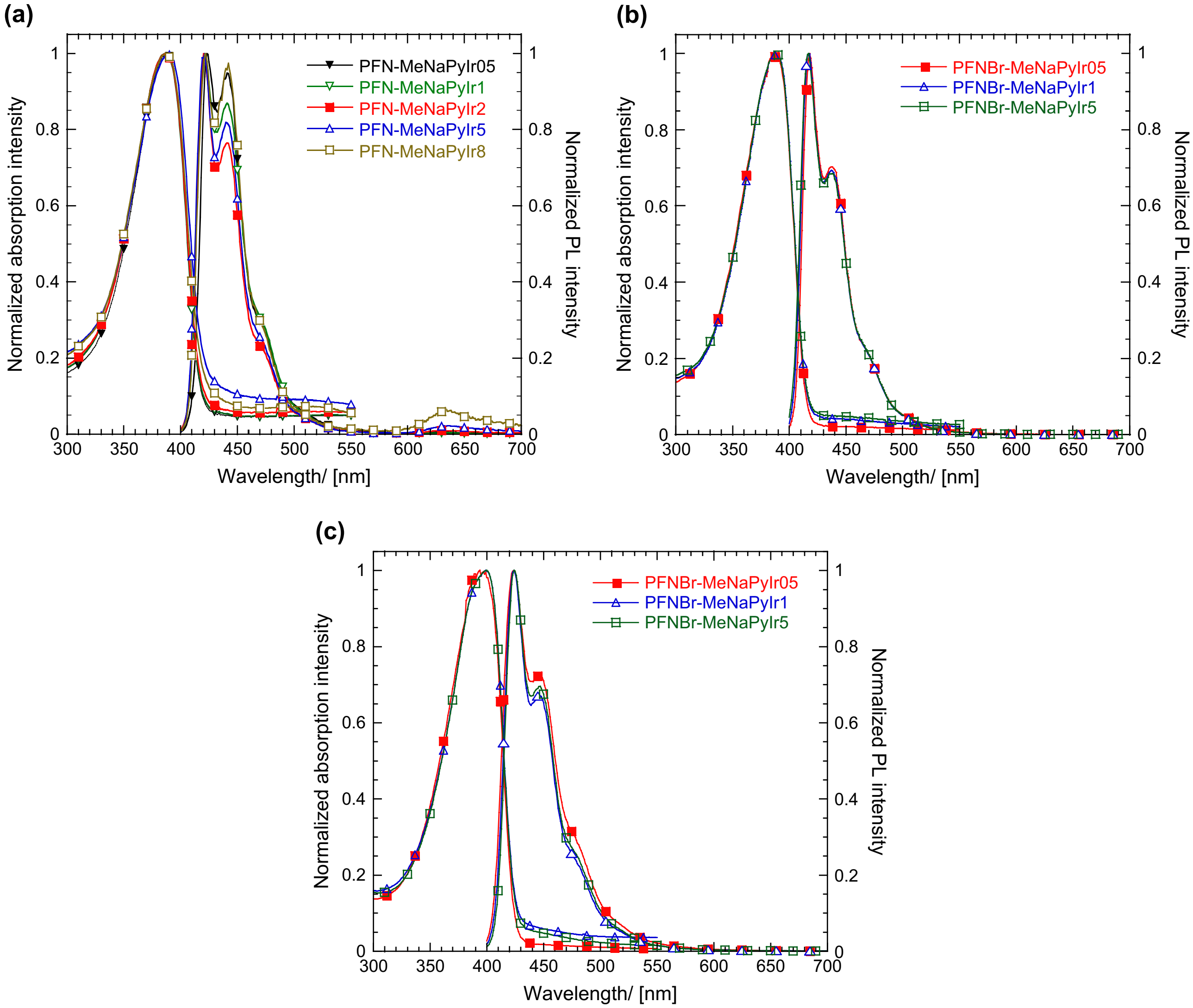


Fig. 2. The UV–vis absorption and PL spectra of PFN–MeNaPyIr in $CHCl_3$ (a) and PFNBr–MeNaPyIr in CH_3OH (b) and DMSO (c).

unit is a faster process and excimer formation can be completely depressed by incorporation of appropriate Ir complex unit in the copolymer main chain.

3.3. Electroluminescent properties

The electroluminescent properties of the neutral and quaternized polymers were investigated with the device structures of ITO/PEDOT:PSS/PVK/polymer/Al and ITO/PEDOT:PSS/PVK/polymer/Ba/Al. It is interesting that these polymers show similar device performance regardless of the cathode being Al or Ba/Al. Many published reports have been focused on the fabrication of devices with a high work function Al cathode, in which a very thin layer of alkali fluorides [36,37], insulating oxides (such as Al_2O_3) [38] or organic surfactants [39–41] were inserted between Al cathode and the light-emitting layer. However, the polymers in this paper can serve as luminescent and electron injection layer at the same time. This phenomenon has been investigated in our previous reports [22,29].

The emissions from the fabricated devices for neutral polymers are dominated by the phosphorescent emission with almost same peak position (642 nm) as in PL spectra of corresponding neutral polymers. Fig. 4a shows the EL spectra of PFN–MeNaPyIr with a device configuration of ITO/PEDOT:PSS/PVK/PFN–MeNaPyIr/Al. The EL spectra with a maximum at ca. 642 nm displayed a saturated red emission. The EL spectra of PFN–MeNaPyIr05 as shown in Fig. 4b with various anode buffer layers and cathodes are almost the same, which indicate that the recombination zone for the devices is located in the light-emitting layer. Almost complete quenching of PFN emission in EL spectra for device from copolymer with Ir complex loading as low as 0.5% (Fig. 4) in contrast to detectable residue PFN emission at around 430 nm for PL spectra of PFN–MeNaPyIr5 film indicates that the dominant mechanisms for the EL emission in neutral polymers is charge trapping rather than Förster energy transfer [14]. Similar charge trapping has been observed in many phosphorescent emission systems [6,7,10,11]. The EL spectra of

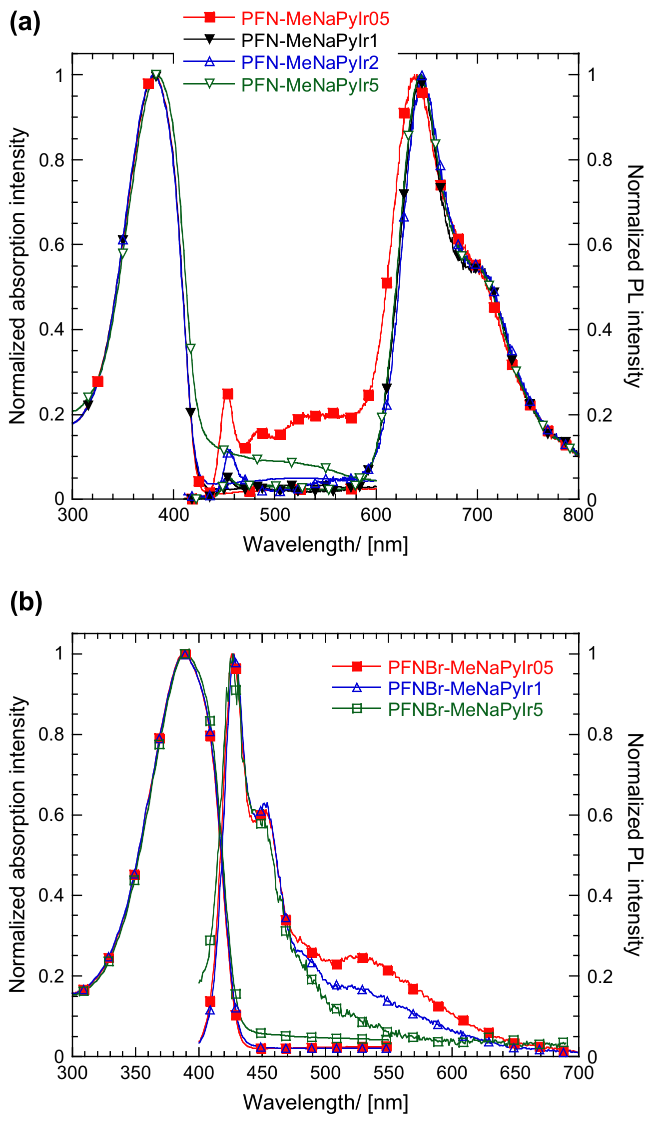


Fig. 3. The UV–vis absorption and PL spectra of PFN–MeNaPyIr (a) and PFNBr–MeNaPyIr (b) in thin film.

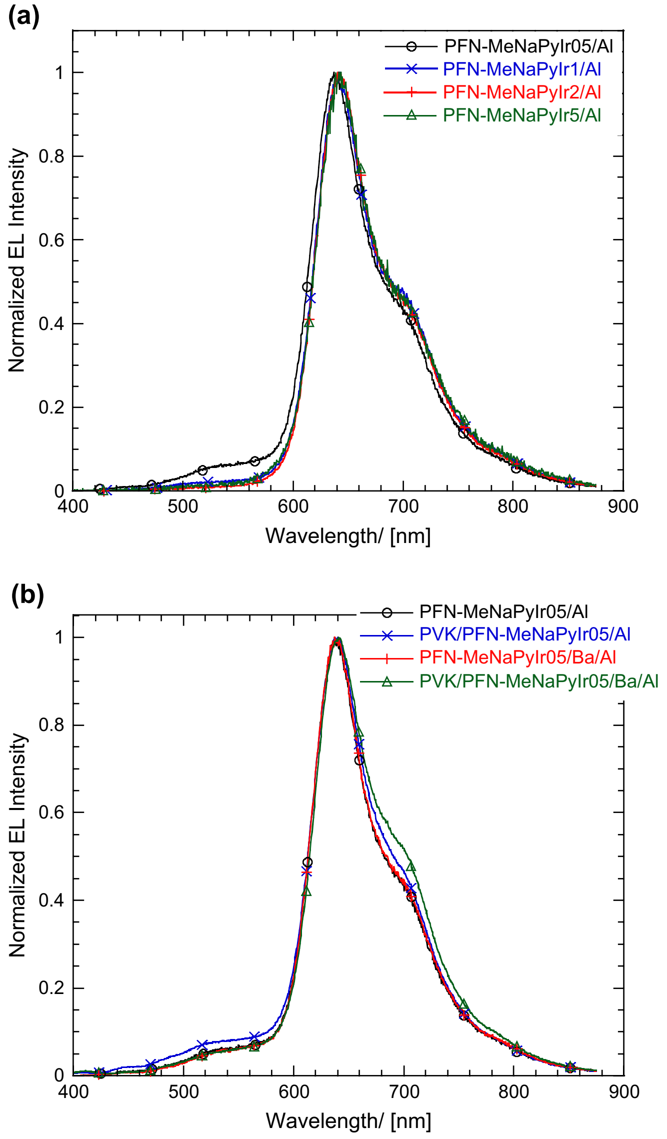


Fig. 4. The EL spectra of (a) PFN–MeNaPyIr with device structure of ITO/PEDOT:PSS/PVK/polymer/Al and (b) PFN–MeNaPyIr05 at different device structures.

PFNBr–MeNaPyIr at device structures of ITO/PEDOT:PSS/PVK/PFNBr–MeNaPyIr5/Al and ITO/PEDOT:PSS/PVK/PFNBr–MeNaPyIr5/Ba/Al are shown in Fig. 5. Similarly, the EL spectra were dominated by the phosphorescent emission peaked at around 645 nm. It is noted that as in case of PL spectra, there is a high-energy broad emission feature at around 535 nm in the EL spectra of PFNBr–MeNaPyIr with both Al and Ba/Al as cathode (inset in Fig. 5), intensity of which decreases with increasing Ir complex content in the quaternized polymers. Again this indicates that the strong probability of excimer formation due to rigid chain conformation of polyelectrolytes [42] and incorporation of 5% Ir complex unit as a trap, are not enough for complete quenching of excimer emission.

The detailed device performance of neutral and quaternized polymers devices are shown in Table 2. PFN–MeNaPyIr05 showed the best device performance. For PFN–MeNaPyIr05, the devices turn on at around 18 V for both Ba/Al and neat Al cathode. The maximum external quantum efficiencies (EQEs) are 0.74% and 0.81%, corresponding to luminance efficiency (LE) of 0.37 cd/A and 0.41 cd/A for Al and Ba/Al cathodes, respectively. The quaternized polymers, PFNBr–MeNaPyIr, showed less efficient device performance [22]. The maximum EQEs of PFNBr–MeNaPyIr05 are reduced to 0.07% and 0.05%, respectively, with Ba/Al and Al as cathode.

4. Conclusions

In this paper, we have synthesized a novel kind of chelating polyfluorene cationic polyelectrolytes and their corresponding precursors with Ir complex incorporated into polymer backbone. Two bromine atoms in different ligands

Table 2
The EL performance of the neutral and quaternized polymers with Ba and Al as cathodes and PVK as the anode buffer layer

Polymer	Cathode	V_{th} (V)	At max EQE				Max B (cd/m^2)
			Volt (V)	B (cd/m^2)	EQE (%)	LE (cd/A)	
PFN−MeNaPyIr05	Al	18.3	19.7	9	0.74	0.37	88
	Ba	18.2	20.8	19	0.81	0.41	93
PFN−MeNaPyIr1	Al	23.2	25.2	17	0.43	0.21	34
	Ba	22.7	25.9	25	0.44	0.22	56
PFN−MeNaPyIr2	Al	23.6	27.1	25	0.66	0.33	78
	Ba	22.8	27.3	16	0.43	0.22	35
PFN−MeNaPyIr5	Al	8.1	12.3	36	0.11	0.05	51
	Ba	7.0	10.4	17	0.05	0.03	28
PFNBr−MeNaPyIr05	Al	11.3	12.6	17	0.05	0.03	36
	Ba	7.9	9.9	15	0.07	0.03	53
PFNBr−MeNaPyIr1	Al	11.7	12.5	14	0.05	0.02	28
	Ba	8.0	10.0	11	0.07	0.03	43
PFNBr−MeNaPyIr5	Al	10.4	11.8	11	0.03	0.01	30
	Ba	9.5	11.0	11	0.04	0.02	28

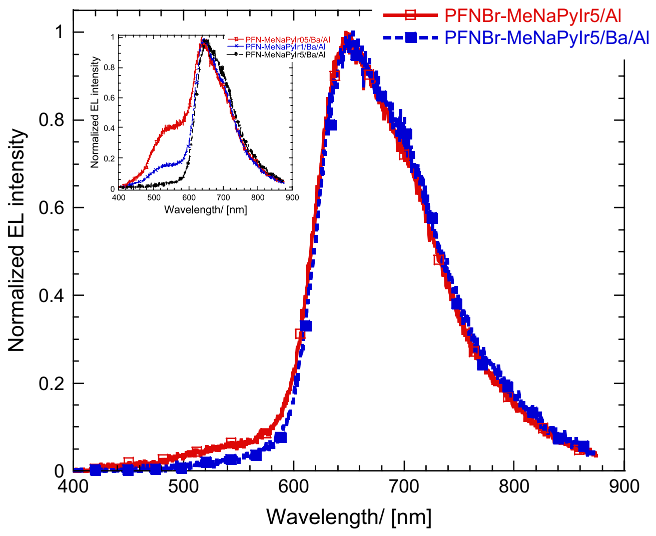


Fig. 5. The EL spectra of PFNBr−MeNaPyIr5 with Ba/Al and Al as cathodes and PVK as the anode buffer layer (inset: the EL spectra of PFNBr−MeNaPyIr with Ba/Al as cathode).

(naphthinatopyridine) of iridium acetylacetonate complex were used as a comonomer in the Suzuki coupling with fluorenes. It results in chelating copolymers with Ir atoms on the polymer backbone. The aminoalkyl or quaternized ammonium group attached to fluorene segment provides good solubility in alcohols and electron injection ability of these phosphorescent polymers with high work function metal cathodes. Devices fabricated from these phosphorescent polymers with air-stable high work function metals, such as Al, as cathode showed comparable device performance with low work function metals, such as Ba. For a neutral polymer PFN−MeNaPyIr05, the maximum external quantum efficiencies (EQEs) and luminance efficiencies (LEs) are 0.74%, 0.37 cd/A and 0.81%, 0.41 cd/A for Al and Ba/Al cathodes, respectively. Unique photoluminescent properties of these chelating polyelectrolyte copolymers and neutral precursor in solution and in solid state film could be good candidate for sensor applications.

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