Chinese Journal of Polymer Science Vol. 35, No. 3, (2017), 342–353

Chinese Journal of Polymer Science
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Institute of Chemistry, CAS
Springer-Verlag Berlin Heidelberg 2017

Synthesis and Photoelectric Properties of New Pr-bonded Polymers by Coordination of Isopropyloxide and Bipyridine Unit*

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Abstract A series of novel praseodymium (Pr)-bonded polymers were successfully synthesized *via* the coordination reaction and palladium-catalyzed Suzuki coupling reaction of 2,7-dibromo-9,9′-dioctylfluorene and different amounts of 5,5′-dibromo-2,2′-bipyridine. The resulting polymers were characterized by ^{1}H-NMR and GPC. The photoluminescence (PL) and electroluminescence (EL) properties of the resulting polymers were studied to explore the effects of the Pr triisopropyloxide. The results showed that the incorporation of Pr into the polymers caused better coplanarity and effective intermolecular or intramolecular interaction, leading to the higher emission intensity at long-wavelength. Further, it was also found that the emission light color could be tuned from blue to green by introduction of a small amount of Pr into the polymer main chain. A single-layer green emitting EL device based on PF(BipyPr)$_6$ with 6 mol% Pr content was fabricated. The device had a low turn-on voltage of 6 V, a brightness of 705.3 cd·m^{-2}, the maximum luminous efficiency of 1.53 cd·A^{-1} and the maximum power efficiency of 0.69 lm·W^{-1}.

Keywords Polyfluorene; Praseodymium; Light-emitting polymers; Bipyridine

INTRODUCTION

Organic conjugated polymers have attracted increasing attention because of their good performances and potential applications in organic light-emitting diode (OLED)[1−5]. Compared with organic small molecules, polymer light-emitting diodes (PLEDs) have the great advantages of ease of fabrication by means of a solution process, low-cost, and ease of covering large areas. A wide range of conjugated polymers such as poly(*p*-phenylenevinylene) (PPV)[6], poly(thiophene) (PT)[7], poly(pyrrole)[8, 9], poly(*p*-phenylene) (PPP)[10], poly(fluorene) (PF)[11, 12] and their derivatives have been extensively investigated as emissive materials in PLED.

Among these conjugated polymers, polyfluorenes with wide-gaps and blue light emission are well-known for their high photoluminescence (PL) efficiency, good chemical and thermal stability, good charge-transporting properties, and facilely structural modification on the carbon-bridge. However, PLEDs based on polyfluorenes as blue-emitting materials generally suffer from undesirable lower-energy emission band under device operation due to reordering of the polymer chains and subsequent excimer formation or ketone-structure in the C-9 position caused by photo-oxidization[13−15]. This leads to the problems of color purity and color stability. Various

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[*] This work was financially supported by the National Natural Science Foundation of China (Nos. 21574021 and 51573026), the Natural Science Foundation of Fujian Province (No. 2015J01189), the Program for Innovative Research Team in Science and Technology in Fujian Province (IRTSTFJ) and the Program of the Education Department of Fujian Province (No. JA14078).

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Received July 29, 2016; Revised September 25, 2016; Accepted September 28, 2016
doi: 10.1007/s10118-017-1909-6

approaches, such as addition of bulky groups[16–18], copolymerization[19], starbranched, hyperbranched structure[20] and metal complexes were explored for stabilizing the emission as well as tuning the color effectively over the visible spectrum[21]. Among them, introduction of a small amount of metal complexes into polyfluorenes has been demonstrated as an efficient approach to tune the emission color and enhance the electroluminescence (EL) of the resulting copolymers. The energy-transfer process takes place in the reported metal-bonded polyfluorenes between the conjugated polyfluorene system and the metal complex. After the conjugated polymer main chain has been excited, energy is transferred to the adjacent low-lying metal-to-ligand-charge-transfer (MLCT) states of the metal complexes. When the metal content increases, the luminescence spectra are dominated by the MLCT emission; meanwhile the $\pi\rightarrow\pi^*$ emission of the polymer main chain quenches. Mostly studied metal complexes applied in PLED are formed by coordination (chelation) of heavy metal (iridium or platinum) or rare-earth-metal (europium, terbium, thulium, dysprosium and erbium) with the ligand (*N*-heterocyclic aromatic, diketone)[22–31].

Rare earth complexes are commonly synthesized by dissolving the ligands in warm ethanol, neutralized to pH = 6 with a base, followed by adding the rare earth metal chloride solution[32]. However, neutralization with aqueous NaOH often leads to the poor solubility of the polymers, and then the partial chelation reaction. To successfully carry out the chelation of the rare earth metal ions in the absence of neutralization, a highly reactive rare earth metal salt, rare earth metal triisopropoxide, was synthesized from anhydrous rare earth metal chloride[33]. The isopropoxy groups of the salt can be easily substituted by chelators, such as bipyridine and phenanthroline, to form a rare earth metal complex in anhydrous organic solvents. In our earlier work, we also found that rare earth metal triisopropyloxide with small polarity could easily coordinate the ligand with the *N*-heterocyclic aromatic structure[32–34]. Meanwhile, they have simpler synthetic step and smaller steric hindrance compared to the above mentioned metal complexes. Lanthanides with energetically close f-levels (Pr, Nd, Ho, Er, Tm, Yb) give rise to emission in the near infrared (NIR) region, rather than the visible region. Here, praseodymium (Pr) was selected due to the smaller molecular weight and lower cost; also, there are few reports in which Pr complexes and Pr-polymers are applied in the OLED. Herein, we designed and synthesized new conjugated Pr-bonded polymers. First, bipyridine (Bipy) unit was introduced into the conjugated polyfluorene backbone as coordination sites. Second, Pr-bonded polyfluorenes were prepared by coordination of the Pr triisopropyloxide and polymers, in which central Pr triisopropyloxide was surrounded by enormous polymer chains. The Pr content in the polymer can be easily adjusted by changing the proportion of the Bipy unit. By controlling the content of Pr, the emission color could be finely tuned from blue to green. In order to explore the effect of the Pr triisopropyloxide on optoelectronic properties, the UV-absorption, photoluminescence and electroluminescence of the resulting polymers were studied.

EXPERIMENTAL

Materials

All the reagents and solvents used in this study were purchased from Sinopharm Chemical Reagent Co. and used without further purification. The monomers 2,7-dibromo-9,9′-dioctylfluorene and 9,9′-dioctylfluorene-2,7-bis(boronic acid pinacol ester) were synthesized according to literature methods[34]. Bipy-Pr complex was synthesized according to a literature method[33].

Measurements

^{1}H-NMR spectra data were expressed in parts per million relative to the internal standard and were obtained on a BRUKER AVIII-400 NMR spectrometer. Pr content was determined by ash method and EDTA titration. UV-Vis absorption spectra in solution or in thin film were obtained on a SHIMADZU UV-2600 spectrometer. The photoluminescence spectra were recorded on a SHIMADZU RF-5301PC. Molecular weight and polydispersity (PDI) of the polymer were determined by gel permeation chromatography (GPC) analysis with polystyrene standard calibration (Waters high pressure GPC assembly model 1515 pump, refractive index detectors, solvent THF). Thermogravimetric analysis (TGA) measurements were performed on a Mettler-Toledo 851e/822e analysis system under O_2 at a heating rate 10 K·min^{-1}. Cyclic voltammetry (CV) measurements were conducted on a CHI600D electro chemical analyzer using a three-electrode cell under N_2 atmosphere. The polymer films on a glassy carbon electrode (working electrode) were scanned anodically and cathodically in a solution of tetrabutylammoniumhexafluorophosphate (n-Bu_4NPF_6) in acetonitrile (0.1 mol·L^{-1}) with Ag/AgCl and a platinum wire as the reference and counter electrode, respectively. The experiments were calibrated with the standard ferrocene/ferrocenium (FOC) redox system with an assumption that the energy level of FOC is 4.8 eV below vacuum, and the value of 0.38 V was found for FOC versus Ag/AgCl. The energy levels of the highest occupied molecular orbital (HOMO) and the levels of lowest unoccupied molecular orbital (LUMO) of the polymers were calculated using the following equations: $E_{\mathrm{HOMO}} = -(E_{\mathrm{ox}}^{\mathrm{onset}} + 4.42)$ eV, $E_{\mathrm{LUMO}} = E_{\mathrm{HOMO}} + E_{\mathrm{g}}^{\mathrm{opt}}$, respectively, where $E_{\mathrm{ox}}^{\mathrm{onset}}$ was the onset potentials for oxidation relative to the AgCl/Ag reference electrode, $E_{\mathrm{g}}^{\mathrm{opt}}$ was the optical band gap of the polymer.

For the measurement of EL, a PLED was made as follows. ITO-coated glass substrates were first thoroughly cleaned in ultrasonic solvent bath and then dried in a heating chamber at 150 °C. Poly(ethylenedioxythiophene) (PEDOT) was spin-coated on the ITO glasses at a speed of 3500 r·min^{-1} for 60 s and then dried at 130 °C for 15 min. The light-emitting polymer layer was then deposited onto the film by spin-coating a polymer solution in chlorobenzene (10 mg·mL^{-1}) at a speed of 2000 r·min^{-1} for 60 s. An electron-transporting layer 2,2′,2″-(1,3,5-benzinetriyl)-tris(1-phenyl-1H-benzimidazole) (TPBI 40 nm) was grown through thermal evaporation using a chamber under pressure of 3×10^{-4} Pa. And then a thin layer of LiF (1 nm) was deposited onto the TPBI layer, followed by aluminum layer (100 nm). Then, the device was encapsulated with UV-curing glue in glove box. The current-voltage and light-intensity measurements were carried. For device characterizations, current-voltage-brightness (*I-V-B*) was measured using a Keithly 2400 source meter and a PR-655 Spectra Scan Spectrophotometers. All the devices fabrication and measurements were carried out under ambient laboratory conditions.

Synthesis of Polymers

The synthetic routes are shown in Scheme 1. A general procedure of polymerization was used for the synthesis of the polymers ($PF(Bipy)_2$, $PF(Bipy)_6$, $PF(Bipy)_{10}$). Under the protection of nitrogen, 2,7-disbromo-9,9′-dioctylfluorene, 9,9′-dioctylfluorene-2,7-bis(boronic acid pinacol ester), 5,5′-disbromo-2,2′-bipyridine, 5.0 mol% $[Pd(PPh_3)_4]$ and toluene, 2 mol·L^{-1} aqueous solution of K_2CO_3 and Aliquat 336 as phase transfer catalyst were added to a round-bottom flask. The mixture was vigorously stirred at 110 °C for 72 h. Bromobenzene was dropped to react for 6 h and phenylboronic acid was dropped to end-cap the polymer for 6 h. After the mixture was cooled to room temperature, it was slowly added dropwise to methanol. A fibrous solid was obtained by filtration. The solid was washed in a Soxhlet extractor with methanol and acetone for 3 d to remove oligomers and catalyst residues. The resulting polymers were collected and dried under vacuum.

PF(Bipy)₂

2,7-Disbromo-9,9′-dioctylfluorene (0.2632 g, 0.4800 mmol), 9,9′-dioctylfluorene-2,7-bis(boronic acid pinacol ester) (0.3223 g, 0.5020 mmol) and 5,5′-disbromo-2,2′-bipyridine (0.0065 g, 0.0207 mmol) were used in polymerization (0.3183 g, 83.0% yield).

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 9.09 (s, ArH), 8.61 (m, ArH), 8.17 (m, ArH), 7.88–7.34 (m, ArH), 2.14 (br, CH_2), 1.61 (br, CH_2), 1.28–1.16 (br, CH_2), 0.99–0.81 (br, CH_3).

PF(Bipy)₆

2,7-Disbromo-9,9′-dioctylfluorene (0.2415 g, 0.4403 mmol), 9,9′-dioctylfluorene-2,7-bis(boronic acid pinacol ester) (0.3222 g, 0.5014 mmol) and 5,5′-disbromo-2,2′-bipyridine (0.0192 g, 0.0612 mmol) were used in polymerization (0.2834 g, 75.7% yield).

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 9.09 (s, ArH), 8.61 (m, ArH), 8.17 (m, ArH), 7.86–7.38 (m, ArH), 2.12 (br, CH_2), 1.59 (br, CH_2), 1.26–1.14 (br, CH_2), 0.88–0.79 (br, CH_3).

PF(Bipy)$_{10}$

2,7-Disbromo-9,9′-dioctylfluorene (0.2200 g, 0.4011 mmol), 9,9′-dioctylfluorene-2,7-bis(boronic acid pinacol ester) (0.3222 g, 0.5014 mmol) and 5,5′-disbromo-2,2′-bipyridine (0.0314 g, 0.1000 mmol) were used in polymerization (0.2842 g, 77.9% yield).

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 9.09 (d, ArH), 8.61 (m, ArH), 8.17 (m, ArH), 7.88–7.32 (m, ArH), 2.14 (br, CH_2), 1.63 (br, CH_2), 1.28–1.16 (br, CH_2), 0.90–0.82 (br, CH_3).

The following procedure was adopted for the synthesis of polymers (PF(BipyPr)$_2$, PF(BipyPr)$_6$, PF(BipyPr)$_{10}$). Pr triisopropoxide was synthesized from anhydrous Pr chloride (Scheme 1). The isopropoxy groups of the salt can be easily substituted by chelators to form a Pr complex in anhydrous organic solvents. Under a nitrogen atmosphere, polymer (0.0500 g), Pr triisopropoxide and toluene were mixed together in a round-bottom flask. After the solid was dissolved, the solution was refluxed for 1 day. The reactant was cooled down to room temperature and was poured into methanol and filtered. The crude product was extracted by Soxhlet extractor with chloroform. The fraction from chloroform was concentrated under reduced pressure and precipitated into methanol. The resulting polymer was collected and dried under vacuum.

PF(BipyPr)$_2$

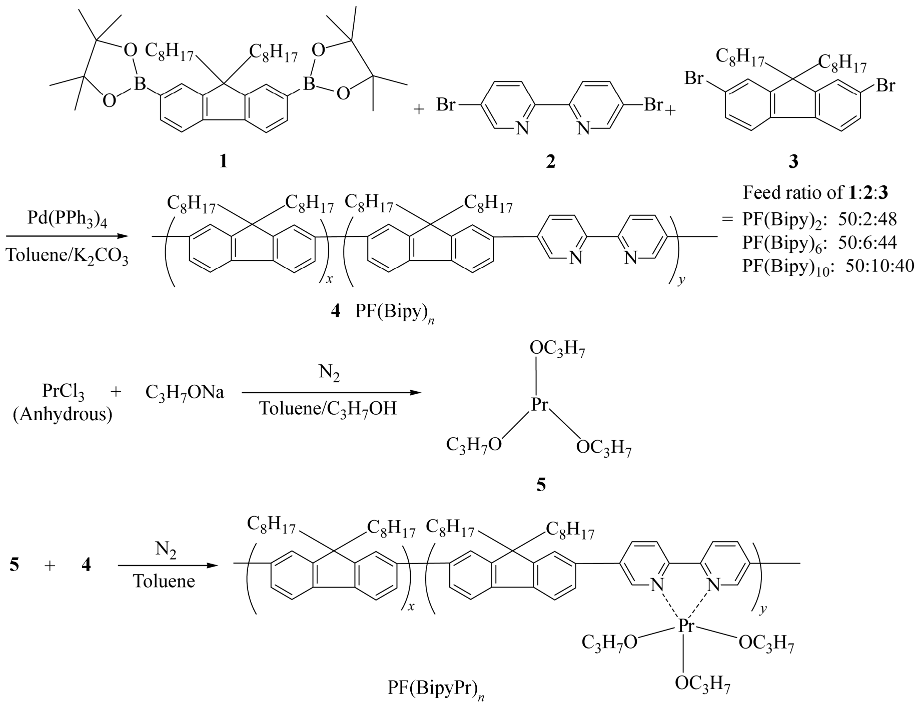
0.0474 g, 93.3% yield; ^{1}H-NMR (400 MHz, $CDCl_3$, δ): 9.07 (s, ArH), 8.58 (m, ArH), 8.11 (m, ArH), 7.86–7.32 (m, ArH), 2.12 (br, CH_2), 1.59 (br, CH_2), 1.26–1.14 (br, CH_2), 0.88–0.80 (br, CH_3).

PF(BipyPr)$_6$

0.0472 g, 90.1% yield; ^{1}H-NMR (400 MHz, $CDCl_3$, δ): 9.12 (br, ArH), 8.57–8.11 (br, ArH), 7.86–7.36 (m, ArH), 2.12 (br, CH_2), 1.64 (br, CH_2), 1.26–1.14 (br, CH_2), 1.00–0.80 (br, CH_3).

PF(BipyPr)$_{10}$

0.0511 g, 94.7% yield; ^{1}H-NMR (400 MHz, $CDCl_3$, δ): 9.07 (d, ArH), 8.60 (m, ArH), 8.11 (m, ArH), 7.86–7.30 (m, ArH), 2.12 (br, CH_2), 1.59 (br, CH_2), 1.26–1.14 (br, CH_2), 0.83–0.72 (br, CH_3).



Scheme 1 Synthetic route and molecular structure of the polymers

RESULTS AND DISCUSSION

Synthesis and Characterization

The polymers consisting of Bipy unit (PF(Bipy)$_2$, PF(Bipy)$_6$, PF(Bipy)$_{10}$) were firstly synthesized by Suzuki coupling reaction and Pr-bonded polymers (PF(BipyPr)$_2$, PF(BipyPr)$_6$, PF(BipyPr)$_{10}$) were synthesized by coordination reaction. The feed ratios of Pr complex in the polymers were 2 mol%, 6 mol% and 10 mol%, and the corresponding polymers were named PF(BipyPr)$_2$, PF(BipyPr)$_6$ and PF(BipyPr)$_{10}$, respectively.

Figure 1 shows the ^{1}H-NMR spectra of PF(Bipy)$_2$, PF(Bipy)$_6$, PF(Bipy)$_{10}$, PF(BipyPr)$_2$, PF(BipyPr)$_6$ and PF(BipyPr)$_{10}$. The signals at approximately δ = 8.11–9.07 correspond to the protons on the Bipy moieties[35], while the peaks at δ = 7.38–7.86 are due to the aromatic protons of fluorene moieties. The peaks at δ = 2.12, 1.59, 1.14–1.26 and 0.79–0.88 are attributed to the alkyl chain of fluorene moieties.

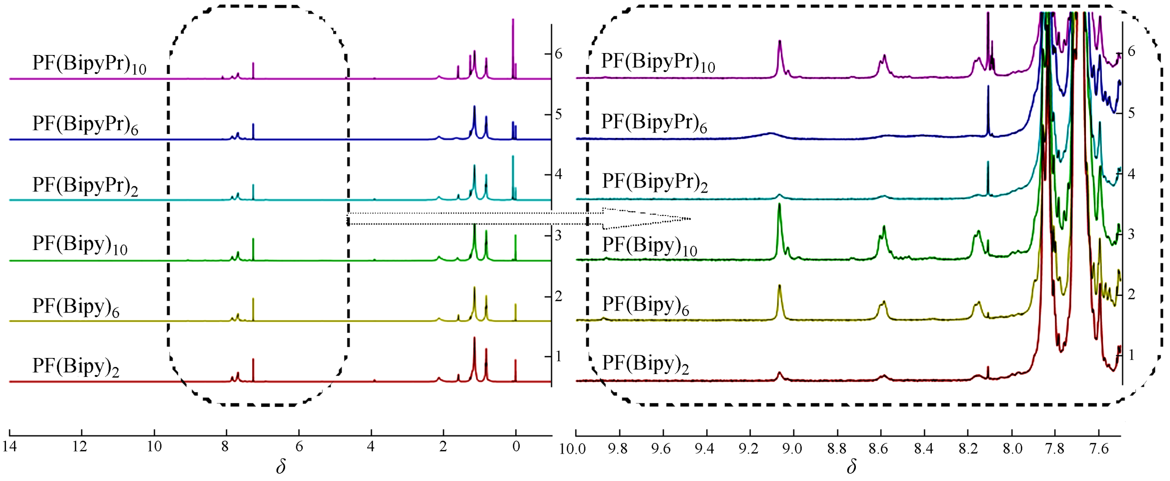


Fig. 1 ^{1}H-NMR spectra of the polymers

As the content of the Bipy units increases, the ^{1}H-NMR spectra exhibit a corresponding enhancement in the intensity of the peaks associated with Bipy, such as the peaks at about δ = 8.11, 8.58 and 9.07 belonging to the aromatic protons of Bipy units. In particular, the ^{1}H-NMR peaks of PF(BipyPr)$_6$ in the low magnetic field region (δ = 8.11–9.10) are very different compared with those of PF(Bipy)$_6$. The proton peaks assigned to the Bipy are broadened and shifted, which may be attributed to the effect of the paramagnetic nature. This indicates that Pr has been incorporated into the polymer by coordination. However, the ^{1}H-NMR signal on OCH of Pr triisopropoxide was not observed in the ^{1}H-NMR spectra of PF(BipyPr)$_n$ due to the low actual Pr content of the polymers. The Bipy content in the conjugated polymers was estimated by the ^{1}H-NMR spectra, which was based on the ratio between the aromatic protons of fluorene (between δ = 7.4 and 8.0) and the Bipy proton peaks. The actual values estimated from the ^{1}H-NMR are shown in Table 1. As the feed ratio increases, so does the actual ratio by an equivalent amount. However, the actual values are lower than the corresponding feed ratio. Pr content in the copolymers was estimated by combining the ash method with EDTA titration data. The results showed that the actual Pr content of polymers was lower than that in the feed ratios. The difference of reaction activity and/or steric hindrance might be responsible for these. The number-average molecular weights (M_n) and weight-average molecular weights (M_w) of the polymers were measured by GPC in THF solvent as shown in Table 1. Compared with Pr-free polymers, Pr-bonded polymers exhibited higher molecular weights. This might be probably explained by the fact that the coordination of Pr and Bipy resulted in the formation of some partial hyperbranched polymer.

Thermal Properties

TGA curves were used to evaluate the thermal properties of the resulting polymers. The corresponding data are summarized in Table 2. Figure 2 shows the TGA thermograms of PF(BipyPr)$_2$, PF(BipyPr)$_6$, PF(BipyPr)$_{10}$ and PF(Bipy)$_6$. The thermal decomposition temperatures (T_d, loss 5 wt%) of PF(BipyPr)$_2$, PF(BipyPr)$_6$, PF(BipyPr)$_{10}$

and PF(Bipy)$_6$ were 298, 315, 315 and 379 °C, respectively, which indicated that all polymers showed good thermal stability with T_d higher than about 298 °C. The introduction of Pr trisorpropyloxide to the polymer decreases the T_d value, which can be attributed to the flexible propyloxide chain.

Table 1 Synthetic results of polymerization

Polymer	Bipy content (mol%)		Pr content (mol%)		M_n ^{c}	M_w ^{c}	PDI
	Feed ratio	Actual ratio ^{a}	Feed ratio	Actual ratio ^{b}			
PF(Bipy)$_2$	2.0	1.9	–	–	1.1×10^4	2.8×10^4	2.52
PF(Bipy)$_6$	6.0	5.7	–	–	2.0×10^4	4.3×10^4	2.11
PF(Bipy)$_{10}$	10.0	7.4	–	–	9.5×10^3	2.5×10^4	2.62
PF(BipyPr)$_2$	–	–	2.0	1.5	1.2×10^4	3.1×10^4	2.50
PF(BipyPr)$_6$	–	–	6.0	3.7	2.2×10^4	4.8×10^4	2.13
PF(BipyPr)$_{10}$	–	–	10.0	5.8	1.2×10^4	3.3×10^4	2.63

^{a} Estimated from the ^{1}H-NMR spectroscopy; ^{b} Estimated from the ash method and EDTA titration; ^{c} Determined by GPC in THF by using a calibration curve of polystyrene standards

Table 2 Thermal, optical and electrochemical properties of polymers

Polymer	CHCl$_3$		Film		$E_g^{opt\ c}$ (eV)	T_d (°C)	E_{ox}^{onset} (V)	E_{HOMO} (eV)	E_{LUMO} (eV)
	λ_{abs} ^{a} (nm)	λ_{em} ^{b} (nm)	λ_{abs} (nm)	λ_{em} (nm)					
PF(Bipy)$_2$	380	416, 441 sh	381	437, 463 sh	2.80	–	1.43	−5.85	−3.05
PF(Bipy)$_6$	380	417, 441 sh	377	436, 468 sh	2.76	379	1.36	−5.78	−3.08
PF(Bipy)$_{10}$	379	418, 439 sh	378	437, 463 sh	2.70	–	1.25	−5.67	−2.91
PF(BipyPr)$_2$	380	416, 441 sh	380	438, 464 sh	2.79	298	1.26	−5.68	−2.89
PF(BipyPr)$_6$	380	416, 440 sh	382	486	2.72	315	1.24	−5.66	−2.94
PF(BipyPr)$_{10}$	379	417, 439 sh	380	435, 463 sh	2.69	315	1.30	−5.72	−3.03

^{a} The maximum absorption wavelength; ^{b} The maximum emission wavelength; ^{c} Optical band gaps calculated from the onset of film absorption

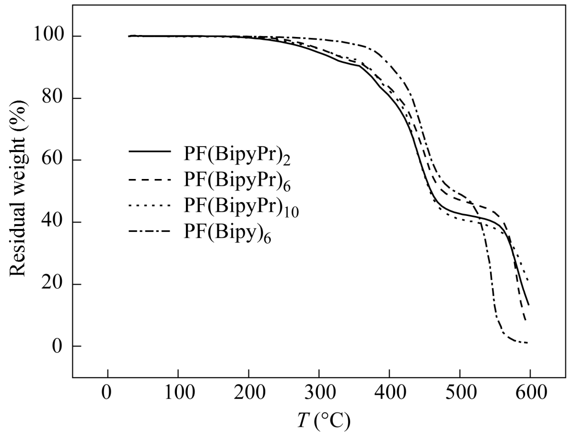


Fig. 2 TGA thermograms of polymers PF(BipyPr)$_2$, PF(BipyPr)$_6$, PF(BipyPr)$_{10}$ and PF(Bipy)$_6$ carried out in oxygen

UV-Vis Absorption Properties and Electrochemical Characteristics

UV-Vis absorption spectra can provide insight into the effective conjugation length and chain conformation of the polymers. In general, the introduction of substituent (either electron donor or electron accepter) on π-electron ring system results in a lower band gap due to the ease of π-electron delocalization. Nevertheless, the band gap of the polymer is dependent not only on the electronic effect of the substituent but also on other parameters, such as coplanarity and twisting of the bulky substituent of the polymer backbone.

The UV-Vis absorption spectra recorded from CHCl$_3$ solutions (approximately 10^{-5} mol·L^{-1}) and thin films are shown in Fig. 3, and the results are summarized in Table 2. The UV-Vis spectra of PF(Bipy)$_2$, PF(Bipy)$_6$, PF(Bipy)$_{10}$, PF(BipyPr)$_2$, PF(BipyPr)$_6$, PF(BipyPr)$_{10}$ in dilute CHCl$_3$ solutions were similar and dominated by a single absorption peak at around 380 nm, almost the same as that of polyfluorene homopolymer[36], which could be attributed to the π-π^* transition from the conjugated polyfluorene backbone.

In thin film, the maximum absorption peaks of $PF(Bipy)_2$, $PF(Bipy)_6$, $PF(Bipy)_{10}$ were 381, 377 and 378 nm, respectively, while the maximum absorption peaks of $PF(BipyPr)_2$, $PF(BipyPr)_6$, $PF(BipyPr)_{10}$ were 380, 382 and 380 nm.

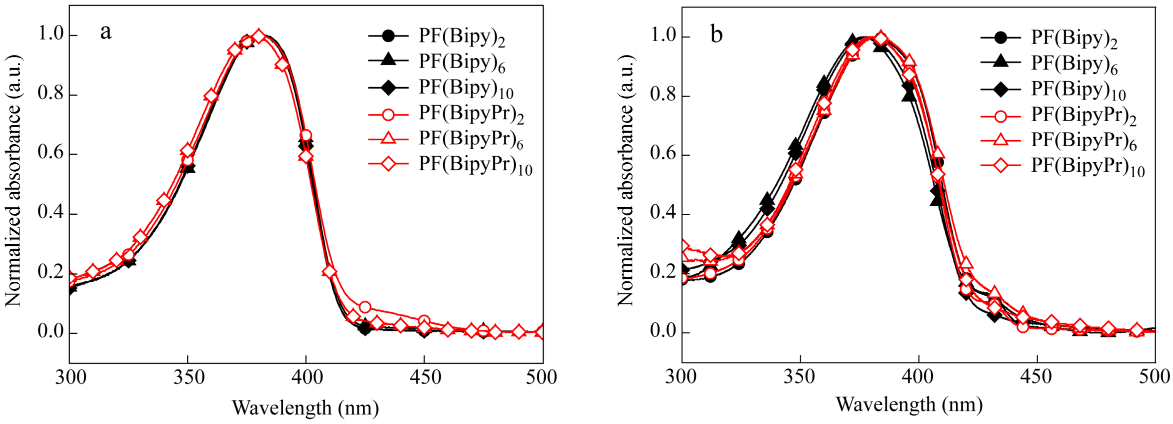


Fig. 3 UV-Vis absorption spectra of polymers: (a) in $CHCl_3$ solution; (b) in films

Because there is approximately a 20° dihedral angle between the two pyridine planes in its transoid-like conformation and the potential barrier for a rotation along the C—C bond connecting the two pyridine rings is small[37], nonplanar conformation could exist in polymers $PF(Bipy)_2$, $PF(Bipy)_6$ and $PF(Bipy)_{10}$. In solution state, the nonplanar conformation has no obvious effect on the absorption spectra of the polymers. In film state, a slight blue shift was observed for $PF(Bipy)_6$ and $PF(Bipy)_{10}$. Generally, PL in film state shows a little bathochromic shift and a certain degree of broadening due to the aggregation of molecules and the stacking of π-π^* bond. However, the PL of $PF(Bipy)_6$ and $PF(Bipy)_{10}$ in thin film state exhibited a slight blue shift compared with the PL in solution state. It might be attributed to the nonplanar conformation due to the 20° dihedral angel between the two pyridine planes of the Bipy unit. Compared with Pr-free polymers ($PF(Bipy)_6$ and $PF(Bipy)_{10}$), Pr-bonded polymers ($PF(BipyPr)_6$ and $PF(BipyPr)_{10}$) restricted the C — C bond rotation, resulting in re-established planar conformation and enhancement of π-conjugation, so the absorption spectra of the two polymers underwent slightly red shift. Moreover, the participation of Pr atom in the polymer backbones might have an effect on the photophysical properties[38].

The optical band gaps of the polymers estimated from the film absorption onset were around 2.69–2.80 eV (Table 2), which were lower than the data reported for polyfluorene homopolymer, 2.95 eV[36]. With the increase of Bipy content in the polymers, the value of the optical band gap of the polymers decreased gradually.

CV analysis was used to study the electrochemical behavior of the resulting polymers and to estimate the HOMO and LUMO energy levels. Figure 4 shows the cyclic voltammograms of polymers films coated on a glassy carbon electrode in a 0.1 $mol\cdot L^{-1}$ n-Bu_4NPF_6-acetonitrile solution. The CV curves were referenced to an AgCl/Ag reference electrode. The results of the electrochemical measurements are listed in Table 2. The Pr-bonded polymers exhibited a slightly decreased oxidation onset compared with corresponding Pr-free polymers[36], which might be attributed to the introduction of Pr triisopropyloxide. The HOMO levels of $PF(BipyPr)_2$, $PF(BipyPr)_6$ and $PF(BipyPr)_{10}$ were −5.68, −5.66, −5.72 eV, respectively, slightly higher than that (−5.80 eV) of polyfluorene homopolymer[36]. From the obtained HOMO levels and the optical band gaps above, it was estimated that the LUMO levels of the polymers $PF(BipyPr)_2$, $PF(BipyPr)_6$ and $PF(BipyPr)_{10}$ were −2.89, −2.94 and −3.03 eV, which decreased with increasing Pr content. It suggested that the incorporation of Pr can increase the electron affinity. However, the LUMO levels of these Pr-bonded polymers were smaller than that of polyfluorene homopolymer (−2.28 eV)[36].

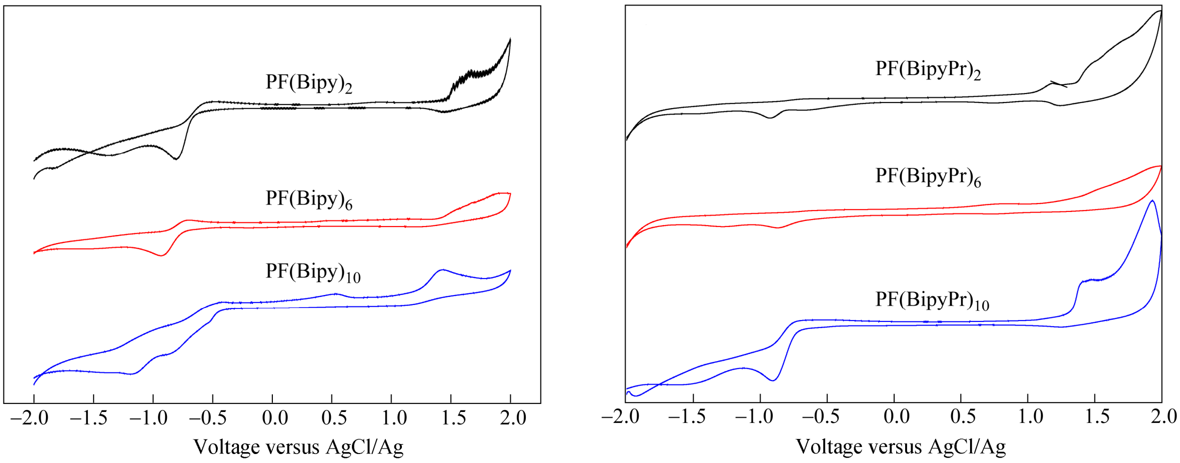


Fig. 4 The CV curves of the polymers: PF(Bipy)$_2$, PF(Bipy)$_6$, PF(Bipy)$_{10}$, PF(BipyPr)$_2$, PF(BipyPr)$_6$ and PF(BipyPr)$_{10}$

Photoluminescence Properties

The PL spectra recorded from CHCl$_3$ solutions (approximately 10^{-5} mol·L^{-1}) and thin films excited at the wavelength of 380 nm are shown in Fig. 5, and the results are summarized in Table 2. The inset of Fig. 5(b) shows the PL spectra of free Bipy-Pr complex excited at the wavelength of 300 nm.

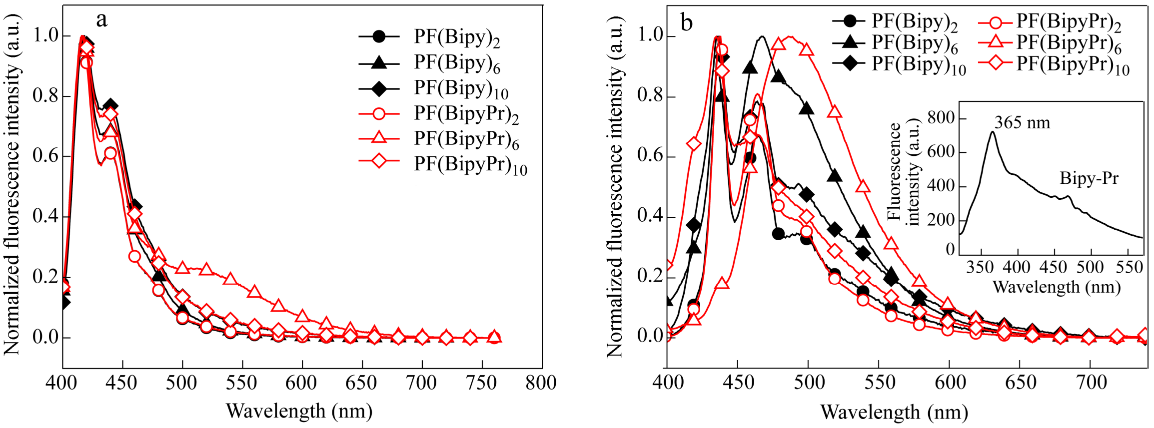


Fig. 5 PL emission spectra of PF(Bipy)$_2$, PF(Bipy)$_6$, PF(Bipy)$_{10}$, PF(BipyPr)$_2$, PF(BipyPr)$_6$ and PF(BipyPr)$_{10}$: (a) in dilute CHCl$_3$ solution; (b) in films (Inset: PL emission spectra of free Bipy-Pr complex)

In CHCl$_3$ solutions, the PL spectra of PF(Bipy)$_2$, PF(Bipy)$_6$, PF(Bipy)$_{10}$, PF(BipyPr)$_2$, PF(BipyPr)$_6$ and PF(BipyPr)$_{10}$ exhibited a sharp emission at 416 nm and a shoulder at about 441 nm, which were associated with the emission from the fluorene segments of the polymers. With the increase of Bipy content in the polymers, the intensity of the emission peak at about 441 nm was enhanced. Moreover, a weak broad peak at 500–550 nm appeared in the PL spectra of PF(BipyPr)$_6$. It indicates that the participation of Pr atom might induce the energy transfer from the excitions created on the fluorene segment to the Bipy-Pr unit.

In thin film, for Pr-free polymers, the emission band from the fluorene segments showed a bathochromic shift by about 20 nm and underwent broadening due to the excimer formation and the closer π-π stacking. In addition, the emission at long-wavelength became stronger than that in solution, which indicated that interchain energy transfer played an important role in solid state. It was noted that the emission intensity at long-wavelength for PF(Bipy)$_6$ was the highest among the three Pr-free polymers, which indicated that the planar conformation and the content of Bipy unit might affect the energy transfer. For Pr-bonded polymer PF(BipyPr)$_6$, the blue polyfluorene emission almost disappeared and only a single broad peak at about 486 nm was observed in solid state. It suggested that the incorporation of Pr might strengthen the intramolecular or intermolecular interaction in solid film, resulting in complete energy transfer from the excited fluorene segment to the Bipy-Pr unit. Because of the rotations along the C—C bond in the Bipy unit of Pr-free polymers, the planar conformation of conjugated polymer backbone was interrupted. For Pr-bonded polymers, the introduction of proper Pr content should lead to better coplanarity of molecular and closer π-π stacking, resulting in strong intramolecular or intermolecular interaction. Further, it can be noted that Pr complex could not emit the visible light (shown in the inset of Fig. 5) and metal-to-ligand-charge-transfer (MLCT) of the metal complexes had not taken place in our Pr-bonded polymers. In addition, the intensity of emission peak at long-wavelength relative to that at short-wavelength increased initially and then decreased with increasing Pr content. With 2 mol% Pr content, the complete energy transfer was not observed for PF(BipyPr)$_2$ due to the lower Pr content. For another, with 10 mol% Pr content, the PL spectrum of PF(BipyPr)$_{10}$ was similar with that of PF(Bipy)$_{10}$, which indicated that the incorporation of higher Pr content had no effect on the PL spectra. It might be the fact that the planarity was distorted by increasing the Bipy unit content resulting in weaker intramolecular or intermolecular interaction. However, the emissions of the polymers were dominated by the competitions of several affected factors.

Electroluminescence Properties and Current-Voltage-Luminance Characteristics

To investigate EL properties of these polymers, devices with the configuration of ITO/PEDOT/Polymer/TPBI/LiF/Al were fabricated, wherein polymers PF(Bipy)$_2$, PF(Bipy)$_6$, PF(BipyPr)$_2$ and PF(BipyPr)$_6$ were used as the emissive layer with corresponding EL spectra shown in Fig. 6.

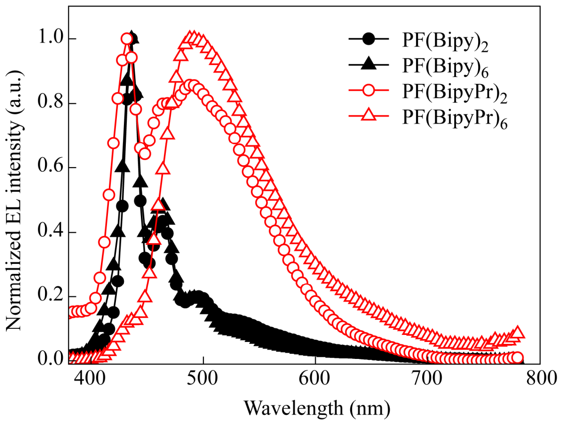


Fig. 6 The EL spectra of the polymers: PF(Bipy)$_2$, PF(Bipy)$_6$, PF(BipyPr)$_2$ and PF(BipyPr)$_6$

Compared with PL of the polymer film, the incorporation of Pr had significant effects on the emission spectra of the polymers in EL devices. The EL spectra of polymers PF(Bipy)$_2$ and PF(Bipy)$_6$ were similar and exhibited blue emission at 432 nm with a weak shoulder at 460 nm. For polymer PF(BipyPr)$_2$ with 2 mol% Pr content, the intensity of the EL emission peak at long-wavelength was obviously enhanced, which was quite different from the corresponding PL spectra. For PF(BipyPr)$_6$, only a single broad EL emission peak at 492 nm (green light) appeared, while blue emission disappeared.

The difference between the PL and EL spectra could be attributed to the differences in recombination zone for photo- and electric excitations. The hole and electron trapping mechanism is most favorable if the HOMO level of the guest is above that of the host and if the LUMO level of the guest is below that of the host[36]. As mentioned in the electrochemical characteristics, the HOMO levels of the PF(BipyPr)$_2$ and PF(BipyPr)$_6$ are higher than that of the polyfluorene homopolymer (host), and the LUMO levels of the PF(BipyPr)$_2$ and PF(BipyPr)$_6$ are lower than that of the host. Hence, energy level alignment of guest (Bipy-Pr unit) and host components in the polymer chain is favorable for intra- and intermolecular trapping in the Pr-bonded polymers PF(BipyPr)$_2$ and PF(BipyPr)$_6$.

Figure 7 shows the current density (J)-voltage-luminance (L) characteristics, J-luminous efficiency (LE) characteristics and *J*-power efficiency (PE) characteristics, wherein polymers PF(Bipy)$_2$, PF(Bipy)$_6$, PF(BipyPr)$_2$ and PF(BipyPr)$_6$ were used as the emissive layer. The relevant device performances are summarized in Table 3. In the context of OLEDs, it is known that intermolecular interactions can quench the luminescence, but would increase wavefunction overlap of the π-electrons and so be beneficial to charge transport[39]. For Pr-bonded polymers, these devices showed much greater performances (higher current density, higher luminance, lower turn-on voltage) compared with Pr-free polymers. The result might be probably caused by higher carrier mobility, which was the result of better coplanarity and closer π-π stacking due to the introduction of Pr. And with the increase of the Pr content (2 mol%–6 mol%), the device performances were better and Commission Internationale d'Eclairage (CIE) showed the emission light to tune from blue to green. Meanwhile, the EL properties of PF(Bipy)$_{10}$ and PF(BipyPr)$_{10}$ have been also investigated. These devices based on polymer PF(BipyPr)$_{10}$ showed poor performances compared with the devices based on polymers PF(BipyPr)$_2$ and PF(BipyPr)$_6$ (the maximum luminance (L_{max}) of 76.6 cd·m^{-2}, the maximum luminous efficiency (LE$_{max}$) of 0.216 cd·A^{-1} and the maximum power efficiency (PE$_{max}$) of 0.097 lm·W^{-1}), which indicated that the incorporation of higher Pr content had no effect on EL properties of the polymers. The best device performances were achieved based on PF(BipyPr)$_6$, which exhibited L_{max} of 705.3 cd·m^{-2}, LE$_{max}$ of 1.53 cd·A^{-1} and PE$_{max}$ of 0.69 lm·W^{-1}. Though the efficiency of device was not high, it could be enhanced by further optimization, such as thermal annealing of emissive layer, choice of solvent and concentration of polymer. However, a new simple synthetic method for rare earth-bonded polymer for PLED was reported for the first time.

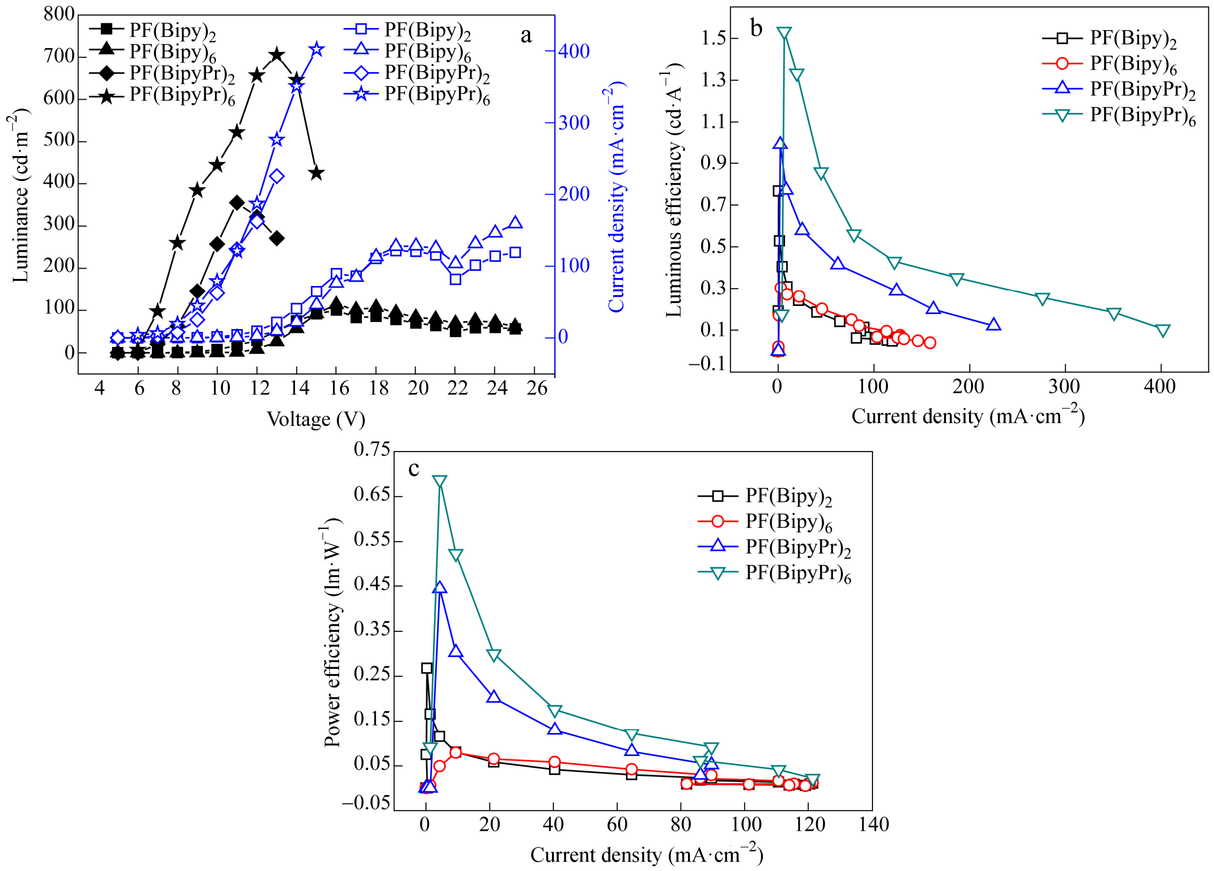


Fig. 7 Current density (open symbols)-voltage-luminance (solid symbols) characteristics (a), current density-luminous efficiency characteristics (b) and current density-power efficiency characteristics (c) of the polymers: PF(Bipy)$_2$, PF(Bipy)$_6$, PF(BipyPr)$_2$ and PF(BipyPr)$_6$

Table 3 EL performances of the polymers

Polymer	CIE coordinates (x, y)	V_{th} (V)	L_{max} ($cd \cdot m^{-2}$)	LE_{max} ($cd \cdot A^{-1}$)	PE_{max} ($lm \cdot W^{-1}$)
PF(Bipy)$_2$	(0.1879, 0.1471)	8	100.4	0.7668	0.2675
PF(Bipy)$_6$	(0.1726, 0.1063)	10	113.8	0.3026	0.0792
PF(BipyPr)$_2$	(0.2153, 0.2749)	6	354.8	0.9912	0.4446
PF(BipyPr)$_6$	(0.2432, 0.4142)	6	705.3	1.5335	0.6879

CONCLUSIONS

A series of novel Pr-bonded polymers based on fluorene unit, Bipy unit and Pr triisopropoxide unit were successfully synthesized by the coordination reaction and Suzuki coupling reaction. The corresponding characterizations and the effects of Pr triisopropoxide on optoelectronic properties have been investigated. The results showed that incorporation of proper Pr content caused better coplanarity and effective intermolecular or intramolecular interaction, leading to color tuning improved device performances. It was found that the introduction of 6 mol% Pr triisopropoxide into polyfluorene structure could effectively tune the emitting color from blue to green. A single-layer green emitting EL device based on PF(BipyPr)$_6$ with 6 mol% Pr content showed a low turn-on voltage of 6 V, a brightness of 705.3 $cd \cdot m^{-2}$, the maximum luminous efficiency of 1.53 $cd \cdot A^{-1}$ and the maximum power efficiency of 0.69 $lm \cdot W^{-1}$. Though the efficiency of device was not high, it can be enhanced by further optimization of conditions. However, a new simple synthetic method for rare earth-bonded polymer for PLED was reported for the first time. The study should be valuable for the design of novel rare earth metal-bonded polymer for optoelectronic applications.

REFERENCES

1 Burroughes, J.H., Bradley, D.D.C., Bown, A.R., Marks, K. and Friend, R.H., Nature, 1990, 347: 539

2 Akcelrud, L., Prog. Polym. Sci., 2003, 28(6): 875

3 Chen, P., Yang, G., Wang, C., Wang, W., Wang, M. and Liu, T., Polym. Int., 2007, 56(8): 996

4 Forrest, S.R., Nature, 2004, 428: 911

5 Kim, D.Y., Cho, H.N. and Kim, C.Y., Prog. Polym. Sci., 2000, 25(8): 1089

6 Greenham, N.C., Moratti, S.C., Bradley, D.D.C., Friend, R.H. and Holmes, A.B., Nature, 1993, 365: 628

7 Roncali, J., Chem. Rev., 1997, 97(1): 173

8 Buschel, M., Ajayaghosh, A., Eldo, J. and Daub, J., Macromolecules, 2002, 35(22): 8405

9 Eldo, J., Arunkumar, E. and Ajayaghosh, A., Tetrahedron Lett., 2000, 41: 6241

10 Anand, K.B., Ashish, A., Tripathi, A.K., Mohapatra, Y.N. and Ajayaghosh, A., Macromolecules, 2007, 40(8): 26578

11 Tour, J.M., Adv. Mater., 1994, 6(3): 190

12 Pei, Q. and Yang, Y.J., J. Am. Chem. Soc., 1996, 118(31): 7416

13 Weinfurner, K.H., Fujikawa, H., Tokito, S. and Taga, Y., Appl. Phys. Lett., 2000, 76(18): 2502

14 Nikitenko, V.R. and Lupton, J.M., J. Appl. Phys., 2003, 93(10): 5973

15 Lemmer, U., Heum, S., Mahte, R.F., Scherf, U., Hopmeier, M. and Siegner, U., Chem. Phys. Lett., 1995, 240(4): 373

16 Ego, C., Grimsdale, A.C., Uckert, F., Yu, G., Srdanov, G. and Mullen, K., Adv. Mater., 2002, 14(11): 809

17 Yu, W.L., Pei, J., Huang, W. and Heeger, A.J., Adv. Mater., 2000, 12(11): 828

18 Miteva, T., Meisel, A., Knoll, W., Nothofer, H.G., Scherf, U. and Muller, D.C., Adv. Mater., 2001, 13(8): 565

19 Zeng, G., Yu, W.L., Chua, S.J. and Huang, W., Macromolecules, 2002, 35(18): 6907

20 Ding, L., Bo, Z., Chu, Q., Li, J., Dai, L. and Pang, Y., Macromol. Chem. Phys., 2006, 207: 870

21 Song, H.J., Kim, D.H., Lee, T.H. and Moon, D.K., Eur. Polym. J., 2012, 48(8): 1485

22 David, M.E., Giulia, T., Silvia, A.R., Kealan, J.F., Franco, C. and Hugo, B., J. Org. Semicond., 2015, 3(1): 1

23 Kido, J., Nagai, K. and Okamoto, Y.J., J. Alloys Compd., 1993, 192: 30

24 Kido, J., Nagai, K. and Ohashi, Y., Chem. Lett., 1990, 657

25 Kido, J. and Okamoto, Y.J., Chem. Rev., 2002, 102(6): 2357
26 Sun, R.G., Wang, Y.Z., Zheng, Q.B., Zhang, H.J. and Epstein, A.J., Appl. Phys., 2000, 87(10): 7589
27 Hong, Z.R., Liang, C.J., Li, R.G., Li, W.L., Zhao, D. and Fan, D., Adv. Mater., 2001, 13(16): 1241
28 Kido, J., Hayase, H., Hongawa, K., Nagai, K. and Okuyama, K., Appl. Phys. Lett., 1994, 65(17): 2124
29 Zhang, K., Chen, Z., Yang, C., Gong, S., Qin, J. and Cao, Y., Macromol. Rapid Commun., 2006, 27(22): 1926
30 Zhao, Q., Cao, T., Li, F., Li, X., Jing, H., Yi, T. and Huang, C., Organometallics, 2007, 26(8): 2077
31 Zhang, K., Chen, Z., Zou, Y., Gong, S., Yang, C., Qin, J. and Cao, Y., Chem. Mater., 2009, 21(14): 3306
32 Ling, Q.D., Kang, E.T., Neoh, K.G. and Huang, W., Macromolecules, 2003, 36(19): 6995
33 Ling, Q.D., Yang, M.J., Wu, Z.F. and Zhang, W., Polymer, 2001, 42(10): 4605
34 Wang, L.H., Wang, W., Zhang, W.G., Kang, E.T. and Huang, W., Chem. Mater., 2000, 12(8): 2212
35 Ng, P.K., Gong, X., Chan, S.H., Lam, L.S.M. and Chan, W.K., Chem. Eur. J., 2001, 7(20): 4358
36 Yang, J., Jiang, C., Zhang, Y., Yang, R., Yang, W., Hou, Q. and Cao, Y., Macromolecules, 2004, 37(4): 1211
37 Chen, L.X., Jäger, W.J.H., Niemczyk, M.P. and Wasielewski, M.R., J. Phys. Chem. A, 1999, 103: 4341
38 Chen, L.X., Jäger, W.J.H., Gosztola, D.J., Niemczyk, M.P. and Wasielewski, M.R., Synth. Met., 2001, 116(1): 229
39 Lupton, J.M., Samuel, I.D.W., Beavington, R., Burn, P.L. and Bässler, H., Adv. Mater., 2001, 13(4): 258