Polymer 50 (2009) 2558-2564

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Efficient white polymer-light-emitting-diodes based on polyfluorene end-capped with yellowish-green fluorescent dye and blended with a red phosphorescent iridium complex

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ARTICLE INFO

Article history: Received 12 February 2009 Received in revised form 19 March 2009 Accepted 22 March 2009 Available online 12 April 2009

Keywords: White-light-emitting-diodes Polyfluorene Iridium complex

ABSTRACT

A novel series of blue and yellowish-green light-emitting single polymers were prepared by end-capping of low contents of 4-bromo-7H-benzo [de]naphtha[2',3':4,5]imidazo[2,1-a]isoquinolin-7-one (M1) into polyfluorene. Electroluminescence (EL) spectra of these polymers exhibit blue emission ($\lambda_{max} = 430/460$ nm) from the fluorene segments and yellowish-green emission ($\lambda_{max} = 510/530$ nm) from the M1 units. For the polymer (PFNAP-0.06) with the M1 unit content of 0.06 mol-%, its EL spectrum shows balanced intensities of blue emission and yellowish-green emission with Commission Internationale de l'Eclairage (CIE) coordinates of (0.25, 0.34). The maximum brightness of the device prepared from the polymer (PFNAP-0.06) is 6704 cd/m² at 10 V with a structure of indium tin oxide (ITO)/poly(3,4-ethyl-enedioxythiophene):poly(styrene sulfonic acid) [PEDOT:PSS]/PVK/emission layer/Ca/Ag. A new white polymer-light-emitting-diode (WPLED) can be developed from the single polymer (PFNAP-0.06) system blended with a red phosphorescent iridium complex [Bis(2-[2'-benzothienyl])-pyridinato-N,C^{3'}] iridium (acetylacetonate) (BtpIr)]. We were able to obtain a white-light-emission device by adjusting the molar ratio of BtpIr to PFNAP-0.06 with a structure of indium tin oxide (ITO)/poly(3,4-ethyl-enedioxythiophene):poly(styrene sulfonic acid) [PEDOT:PSS]/PVK/emission layer/Ca/Ag. The brightness in such a device configuration is 4030 cd/m² at 9 V with CIE coordinates of (0.32, 0.34).

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1. Introduction

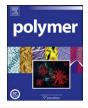
Recently, many studies have been focused on white polymerlight-emitting-diodes (WPLEDs) because of their potential applications in back-lighting for liquid-crystal displays, full-color displays with a color filter, and lighting sources [1–4]. The general approach to obtain WPLEDs is to blend fluorescent or phosphorescent dyes into a polymer matrix [5–13] or to use polymer blending systems, such as blending red-, green-, and blue-light-emitting polymers or blue-, and orange-light-emitting polymers [14–19]. The light from a dye-doped polymer acting as a single emissive layer can emit a white color through control of the doping level [20–22]. These single-layer polymer blending systems have simple device structures. It is utilized widely to generate white light.

Meanwhile, electrophosphorescent polymers have also attracted much research interest due to their high quantum efficiency. Both singlet and triplet excitons can be fully utilized in electrophosphorescence, because of the strong spin–orbital coupling effect of heavy metal ions in the phosphorescent complexes. Therefore, a maximum of 100% internal quantum efficiency can be achieved theoretically [23–29]. There are many studies focused on electrophosphorescent polymers based on iridium complexes owing to their high luminous efficiency.

Polymers with large bandgaps can be used as blue light sources in full-color displays or host materials for lower-energy fluorescent or phosphorescent dyes. Polyfluorenes (PFs) emit in the blue region. PFs are very promising materials for light-emitting materials because of their high photoluminescence (PL) and electroluminescence (EL) efficiencies and high thermal stabilities. We can change the emitting colors of PFs through the introduction of lowbandgap monomers into the polymer backbone [30–32]. PFs can be used as host materials to blend with other conjugated polymers, fluorescent dyes, and organometallic triplet emitters. Then, we can generate other colors through energy transfer from fluorene segments to lower-energy emitters [33,34]. Consequently, PFs can be used as both the host and the blue emitter in WPLEDs.

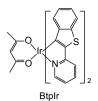
In our research, a novel series of blue and yellowish-green lightemitting single polymers have been prepared by incorporation of low contents of 4-bromo-7H-benzo[de] naphtha[2',3':4,5]imidazo[2,1a]isoquinolin-7-one (M1) into polyfluorene by end-capping method.





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^{0032-3861/\$ -} see front matter \odot 2009 Elsevier Ltd. All rights reserved. doi:10.1016/j.polymer.2009.03.051



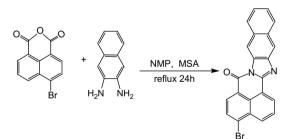
Scheme 1. The chemical structure of Btplr.

To the best of our knowledge, this is the first report of polyfluorene containing 4-bromo-7H-benzo[de]naphtha[2',3':4,5]imidazo [2,1alisoquinolin-7-one (M1). Electroluminescence (EL) spectra of these polymers exhibit blue emission ($\lambda_{max} = 430/460$ nm) from the fluorene segments and yellowish-green emission ($\lambda_{max} = 510/530$ nm) from the M1 units. Energy transfer from fluorene segments to M1 units was observed. The vellowish-green emission band came from the energy transfer and charge trapping from the fluorene segments to the M1 units. With the increase of the M1 unit's content in the polymer, the relative intensity of the yellowish-green emission band in the EL spectra became stronger, due to the more complete energy transfer and charge trapping. We have achieved a new type of electrophosphorescent WPLEDs from the polymers blended with a red phosphorescent iridium complex [bis(2-[2'-benzothienyl)-pyridinato-N,C^{3'}]iridium(acetylacetonate)(BtpIr)]. The structure of BtpIr is shown in Scheme 1.

2. Experimental

2.1. Instrumentation

The IR spectra were recorded on a Jasco 460 FTIR spectrometer. ¹H NMR spectra were collected on a Brucker Avance 600 spectrometer. Molecular weight determination was obtained by using a Waters GPC 2414 in tetrahydrofuran (THF) via a calibration curve of polystyrene standards. Thermal stability was analyzed using a TA Instrument Thermogravimetric Analyzer (TGA) Q500 at a heating rate of 10 °C/min under nitrogen. The glass transition temperature (Tg) was determined on a TA Instruments Model 2920 Differential Scanning Calorimeter (DSC) at a heating rate of 20 °C/min under



Scheme 2. Synthesis of monomer (M1).

nitrogen. Ultraviolet–visible (UV–vis) absorption spectra were recorded on a Hitachi U-2001 spectrophotometer. Photoluminescent (PL) spectra were measured by a Hitachi F-4500 fluorescence spectrometer. Electroluminescent (EL) spectra and luminance of the devices were measured using a Photoresearch PR650. The voltage–current was controlled by a Keithley 2400 power source. Cyclic voltammetry was carried out on a potentiostat/galvanostat model 283 (Princeton Applied Research) with a platinum electrode at a scan rate of 50 mV/s against Ag/AgCl reference electrode with nitrogen-saturated solution of 0.1 M tetran-butylammonium perchlorate $[CH_3(CH_2)_3]_4N \cdot ClO_4$ in acetonitrile. Ferrocene (FOC) was used as the internal standard.

2.2. Materials

2,7-Dibromo-9,9-dioctylfluorene, polyvinylcarbazole (PVK), 2,3-diaminonaphthalene, 4-bromo-1,8-naphthalicanhydride, 2,2dipyridyl, methanesulfonic acid (MSA), 1,5-cyclooctadiene, bis(1,5cyclooctadiene)nickel(0) [Ni(COD)₂] were obtained from Aldrich. Toluene and N,N-dimethylformamide (DMF) were purchased from TEDIA, and distilled over calcium hydride. O-xylene, chloroform, dichlorobenzene and 1-methyl-2-pyrrolidinone (NMP) were also purchased from TEDIA. Bis(2-[2'-benzothienyl)-pyridinato-N,C^{3'}] iridium (acetylacetonate) (BtpIr) was purchased from American Dye Source, Inc.

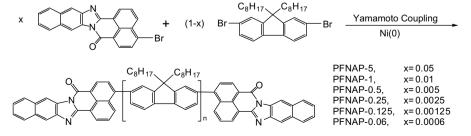
2.3. Synthesis of monomer

2.3.1. 4-Bromo-7H-benzo[de]naphtha[2',3':4,5]imidazo[2,1-a]isoquinolin-7-one (M1)

The synthetic route is shown in Scheme 2. To a 100 mL roundbottom flask containing 1 g (3.6 mmol) of 4-bromo-1,8-naphthalic anhydride in 30 mL of NMP, 0.57 g (3.6 mmol) of 2,3-diaminonaphthalene was added. Two drops of methanesulfonic acid (MSA) were added as a catalyst. Then the mixture was slowly heated to 100 °C, and kept at that temperature for half an hour. The mixture was heated to the temperature of reflux, and maintained at that temperature for another 24 h. After 24 h, the dark-red reaction mixture was cooled to room temperature, and an orange product precipitated out from the reaction mixture. The product was isolated by filtration, and washed with a minimum amount of NMP followed by recrystallization from NMP. The solid was dried in vacuum at 130 °C for 24 h. An orange powder M1 was obtained, and the yield was 85%; mp: 297 °C. FT-IR: 1700 cm⁻¹ (C=O). ¹H NMR (600 MHz, DMSO-d₆, ppm): 7.55 (t, 2H), 8.06-8.12 (m, 4H), 8.31 (t, 1H), 8.41 (s, 1H), 8.54-8.8 (m, 2H), 8.9 (m, 1H). Elemental analysis (%) calcd: C, 66.16; H, 2.74; N, 7.01; Found: C, 65.9; H, 2.76; N, 6.91.

2.4. General procedures of polymers' synthesis

The synthetic route of the polymers is shown in Scheme 3. All polymers were synthesized in the same way. The PFNAP-5 is taken as



Scheme 3. Synthesis of polymers.

Table 1
Molecular weight, polydispersity and thermal properties of polymers.

Polymer	Content of M1	$\begin{array}{c} Mn \\ (g/mol) \times 10^4 \end{array}$	$\begin{array}{c} Mw \\ (g/mol) \times 10^4 \end{array}$	PDI	T _g (°C)	T _{5d} (°C) ^a
PFNAP-5	0.05	1.71	2.86	1.67	110	416
PFNAP-1	0.01	1.68	2.65	1.57	106	410
PFNAP-0.5	0.005	1.98	2.86	1.44	106	410
PFNAP-0.25	0.0025	1.32	2.25	1.69	101	409
PFNAP-0.125	0.00125	1.38	2.34	1.68	98	416
PFNAP-0.06	0.0006	2.25	3.16	1.40	90	404

^a Temperature of 5% weight loss measured by TGA in nitrogen.

an example. To a 100 mL round-bottom flask, Ni(COD)₂ (2 g, 7.11 mmol), 2,2-dipyridyl (1.11 g, 7.11 mmol) and 1,5-cyclooctadiene (0.768 g, 7.11 mmol) were dissolved in 10 mL of DMF under a nitrogen atmosphere. The solution was heated to 80 °C for half an hour to form a purple complex. 2,7-Dibromo-9,9-dioctylfluorene 1.51 g (2.75 mmol) and M1 58 mg (0.145 mmol), in a mixture of 20 mL of toluene and 5 mL of DMF, were added to the solution, and heated at 80 °C for another 3 days. After being cooled to room temperature, the reaction mixture was poured into a mixture of 200 mL of HCl. 200 mL of acetone and 200 mL of methanol, which was stirred for 2 h. The solid was filtered, and redissolved in chloroform. Then it was precipitated in a large amount of methanol. The solid was purified by a Soxhlet extractor for 24 h using acetone as the solvent, and dried in a vacuum oven at 70 °C overnight. The yield was 80%; ¹H NMR (600 MHz, CDCl₃, ppm): 0.83 (t, 6H), 1.2 (broad, 24H), 2.13 (broad, 4H), 7.63–7.85 (broad, Ar-H), 8–9 (broad, weak peaks of M1 units). Elemental analysis (%) calcd: C, 89.53; H, 10.03; N, 0.36; Found: C, 89.21; H, 10.01; N, 0.3.

2.4.1. PFNAP-1

Monomer feed ratio: 2,7-dibromo-9,9-dioctylfluorene 1.51 g (2.75 mmol) and M1 11 mg (0.0275 mmol). The yield was 75%; ¹H NMR (600 MHz, CDCl₃, ppm): 0.83 (t, 6H), 1.2 (broad, 24H), 2.13 (broad, 4H), 7.63–7.85 (broad, Ar–H). Elemental analysis (%) calcd: C, 89.63; H, 10.25; Found: C, 89.41; H, 10.21.

2.4.2. PFNAP-0.5

Monomer feed ratio: 2,7-dibromo-9,9-dioctylfluorene 1.51 g (2.75 mmol) and M1 5.5 mg (0.0137 mmol). The yield was 77%; 1 H NMR (600 MHz, CDCl₃, ppm): 0.84 (t, 6H), 1.2 (broad, 24H), 2.15

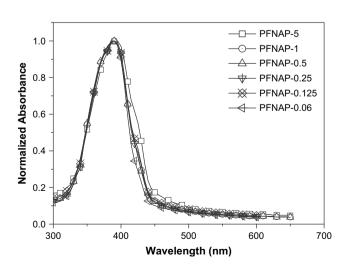


Fig. 1. UV-vis absorption spectra of the polymers in solid films.

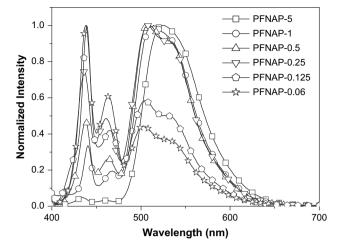


Fig. 2. PL emission spectra of the polymers in solid films.

(broad, 4H), 7.63–7.85 (broad, Ar–H). Elemental analysis (%) calcd: C, 89.66; H, 10.28; Found: C, 89.55; H, 10.35.

2.4.3. PFNAP-0.25

Monomer feed ratio: 2,7-dibromo-9,9-dioctylfluorene 1.51 g (2.75 mmol) and M1 2.73 mg (0.00685 mmol). The yield was 76%; ¹H NMR (600 MHz, CDCl₃, ppm): 0.85 (t, 6H), 1.18 (broad, 24H), 2.12 (broad, 4H), 7.63–7.85 (broad, Ar–H). Elemental analysis (%) calcd: C, 89.67; H, 10.29; Found: C, 89.33; H, 10.32.

2.4.4. PFNAP-0.125

Monomer feed ratio: 2,7-dibromo-9,9-dioctylfluorene 1.51 g (2.75 mmol) and M1 1.36 mg (0.00342 mmol). The yield was 70%; ¹H NMR (600 MHz, CDCl₃, ppm): 0.84 (t, 6H), 1.2 (broad, 24H), 2.15 (broad, 4H), 7.63–7.85 (broad, Ar–H). Elemental analysis (%) calcd: C, 89.68; H, 10.30; Found: C, 89.54; H, 10.23.

2.4.5. PFNAP-0.06

Monomer feed ratio: 2,7-dibromo-9,9-dioctylfluorene 1.63 g (2.97 mmol) and M1 0.7 mg (0.00178 mmol). The yield was 81%; ¹H NMR (600 MHz, CDCl₃, ppm): 0.83 (t, 6H), 1.2 (broad, 24H), 2.14 (broad, 4H), 7.63–7.85 (broad, Ar–H). Elemental analysis (%) calcd: C, 89.68; H, 10.30; Found: C, 89.51; H, 10.19.

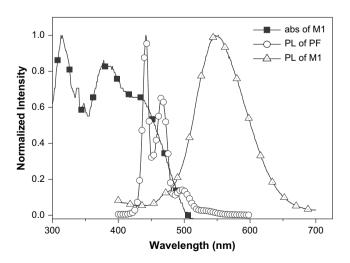


Fig. 3. PL emission spectra of M1 (in DMAc) and polyfluorene film, and UV-vis absorption spectrum of M1 dissolved in DMAc.

Table 2Electrochemical properties of polymers.

Polymer	E _{ox,onset}	E _{red,onset}	E _{ox,onset} vs FOC	E _{ox,onset} vs FOC	HOMO (eV)	LUMO (eV)	Eg (eV)
PFNAP-5	1.36	-1.98	0.90	-2.44	-5.70	-2.36	3.34
PFNAP-1	1.39	-1.97	0.93	-2.43	-5.73	-2.37	3.36
PFNAP-0.5	1.36	-2.08	0.90	-2.54	-5.70	-2.26	3.44
PFNAP-0.25	1.35	-2.10	0.89	-2.56	-5.69	-2.24	3.45
PFNAP-0.125	1.39	-2.08	0.93	-2.54	-5.73	-2.26	3.47
PFNAP-0.06	1.40	-2.09	0.94	-2.55	-5.74	-2.25	3.49

 $E_{FOC}\,{=}\,0.46~V~vs~Ag/Ag{+}.$

 $E_{HOMO} = -e(E_{ox,onset vs FOC} + 4.8 V).$

 $E_{LUMO} = -e(E_{red,onset vs FOC} + 4.8 V).$

2.5. WPLED blending system (PFNAP-0.06 blended with 1 mol-% BtpIr)

PFNAP-0.06 (0.03 g) and BtpIr (0.54 mg) were dissolved in 3 mL of o-xylene for the emission layer of the PLED device.

2.6. Light-emitting devices fabrication

Polymers were dissolved in o-xylene and filtered through a 0.45 µm filter. Patterned indium tin oxide (ITO) glass was cleaned with acetone, 2-propanol and de-ionized water in an ultrasonic bath, and dried on a hot plate at 130 °C for 10 min, and then treated with UV Ozone for 30 min before use. A 30 nm hole injection layer of poly-(styrene sulfonic acid) doped poly(ethylene dioxythiophene) [PEDOT:PSS] (Baytron P CH 8000, Bayer AG, Germany) was spincoated on the ITO, and baked for 30 min at 130 °C. Then, a 20 nm thick layer of PVK, used as a hole-transportation layer, was spin-coated from a dichlorobenzene solution (5 g/L), and dried for 30 min at 130 °C. Then, the ITO glass was cooled to room temperature, and laid in glass Petri dish overnight. On the top of it, the 60–80 nm emitting polymer was spin-coated from its solution in o-xylene (10 g/L). Finally, a thin layer of calcium (10 nm) was deposited by thermoevaporation under a vacuum of 10^{-5} torr and followed by a layer of silver (150 nm). The device fabrication was carried out in air at room temperature, and was tested in a glove box (H_2O , $O_2 < 1$ ppm).

3. Results and discussion

Normalized Intensity

400

3.1. Synthesis and characterization of the polymers

4-Bromo-7H-benzo[de]naphtha[2',3':4,5] imidazo[2,1-a]isoquinolin-7-one (M1) was synthesized from the condensation

Fig. 4. EL spectra of the electroluminescent devices of the polymers.

Wavelength (nm)

500

Та	ble 3	
EL	nrono	rtion

EL	pro	per	ties	01	por	ymers	•

Polymer	Turn-on voltage (V)	Brightness max (cd/m ²)	Luminous efficiency max (cd/A)	CIE (x, y)
PFNAP-5	7	6534	0.56	(0.36, 0.56)
PFNAP-1	6	13,300	1.1	(0.36, 0.56)
PFNAP-0.5	4.5	26,200	1.49	(0.33, 0.54)
PFNAP-0.25	4	11,400	1.5	(0.32, 0.51)
PFNAP-0.125	4	11,600	1.93	(0.29, 0.47)
PFNAP-0.06	4	6704	0.87	(0.25, 0.34)
PFNAP-0.06 blended with 1 mol-% BtpIr	4	7050	0.75	(0.32, 0.34)

reaction of 4-bromo-1,8-naphthalic anhydride and 2,3-diaminonaphthalene. Methanesulfonic acid was used as the catalyst. The yield of the reaction was 85%. The polymerization reactions were carried out via a Yamamoto polycondensation reaction with Ni(0) as the catalyst. M1 was introduced to the polymers by end-capping. The amount of M1 added to the polymerization ranged from 5 mol-% to 0.06 mol-% (Scheme 3). The weight-average molecular weights (Mw) of these polymers are from 22,500 to 31,600 g/mol, and the number-average molecular weights (Mn) are from 13,200 to 22,500 g/mol. The polydispersity indexes (Mw/Mn) (listed in Table 1) of these polymers are typical for a polycondensation reaction. All polymers are soluble in common organic solvents, such as chloroform, o-xylene, THF, and toluene. These polymers' chemical structures were verified by ¹H NMR and elemental analysis. The signal at 8–9 ppm in ¹H NMR spectra and the N contents from elemental analysis are attributed to the M1 units, and the M1 unit's actual contents in the polymers could be calculated. The actual content of M1 units in PFNAP-5 is 4.2 mol-%, which is to some extent, close to the feed ratio in the polymerization. For PFNAP-1, PFNAP-0.5, PFNAP-0.25, PFNAP-0.125, and PFNAP-0.06, the contents of M1 units are too low to give signals in ¹H NMR and elemental analysis.

The thermal stability of these polymers was determined by TGA under nitrogen as shown in Table 1. The 5% weight loss temperatures (T_{5d}) of polymers ranged from 404 to 416 °C (Table 1). These data indicate that all polymers have good thermal stabilities. Glass transition temperatures (T_gs) of polymers were investigated by DSC under nitrogen. The T_gs of the polymers are in the range of 90–110 °C

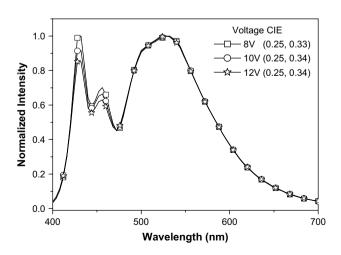
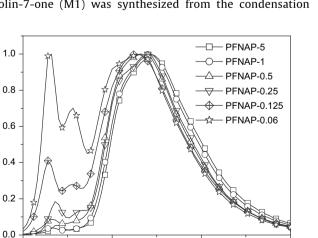


Fig. 5. EL spectra of the electroluminescent devices of PFNAP-0.06 under different bias conditions with corresponding CIE coordinates.



600

700

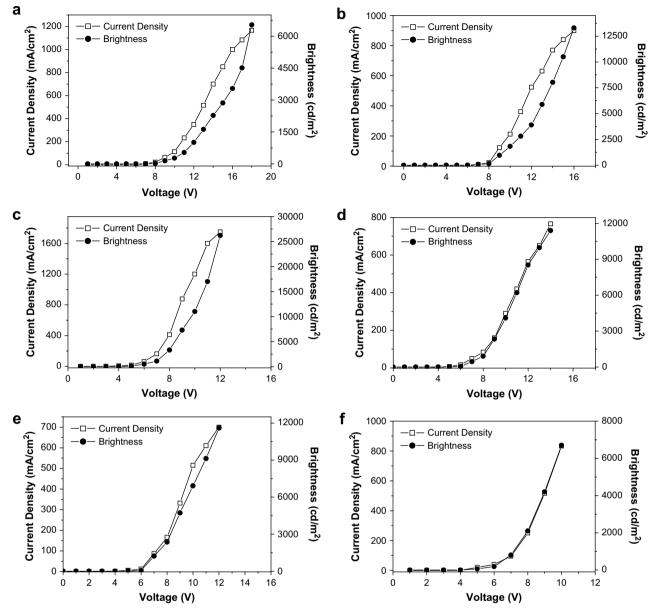


Fig. 6. I-V-B curves of polymers: (a) PFNAP-5, (b) PFNAP-1, (c) PFNAP-0.5, (d) PFNAP-0.25, (e) PFNAP-0.125, and (f) PFNAP-0.06.

(Table 1). All polymers have higher T_gs than pure polyfluorene ($T_g = 76$ °C), which is due to the M1 units having a rigid molecular structure. The rigid molecular structure limits the motion of polymer chains. The T_gs of polymers increase with the increasing content of M1 units from 90 °C (PFNAP-0.06) to 110 °C (PFNAP-5).

3.2. Optical properties

The absorption spectra of the polymer films are shown in Fig. 1. The UV–vis spectra of the polymers are dominated by an intense peak at around $\lambda_{max} = 390$ nm, which comes from the π – π^* transition of the fluorene units in the polymer backbone. The absorption peaks of M1 units could not be observed from the spectra, because their content in the polymer chain is quite low. Fig. 2 shows the PL spectra of the polymers in solid films with an excitation wavelength of 380 nm. All the PL spectra of the polymers exhibit two emission bands at $\lambda_{max} = 437/463$ nm and

 $\lambda_{max} = 510/530$ nm, which are assigned to the fluorene segments and the M1 units, respectively. The emission band of M1 units comes from the Förster energy transfer from polyfluorene to the M1 units, due to the overlap of the PL spectrum of polyfluorene and UV–vis spectrum of the compound M1 (Fig. 3). With the increase of the M1 unit's content, the relative intensities of the band at $\lambda_{max} = 510/530$ nm increase because of the more efficient energy transfer. The yellowish-green emission band in the PL spectra of PFNAP-5 and PFNAP-1 is red-shifted compared with other polymers because of the aggregation of M1 units at high M1 concentration.

3.3. Electrochemical properties

The electrochemical properties of the polymers were investigated by cyclic voltammetry (CV). All polymers show similar redox properties with one oxidation process and one reduction process.

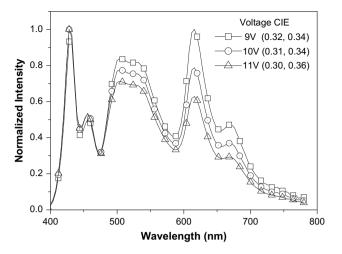


Fig. 7. EL spectra of the electroluminescent devices of PFNAP-0.06 blended with 1 mol-% Btplr under different bias conditions with corresponding CIE coordinates.

According to the formula, $E_{FOC} = 0.46 \text{ V}$ vs Ag/Ag+; $E_{HOMO} = -e$ ($E_{ox,onset}$ vs $_{FOC} + 4.8 \text{ V}$); $E_{LUMO} = -e(E_{red,onset}$ vs $_{FOC} + 4.8 \text{ V}$), we estimated the HOMO and LUMO energy levels of the polymers to be -5.69 to -5.74 eV and -2.24 to -2.37 eV, respectively (Table 2). The results show that the energy levels of the polymers have slight changes than that of pure polyfluorene [35].

3.4. Electroluminescence (EL) properties of the devices

The devices were fabricated in the configuration of ITO/ PEDOT:PSS/PVK/emission layer/Ca/Ag. In order to lower the barrier for electron injection, low work function calcium was chosen as the cathode. However, low work function metals are air sensitive, so an additional layer of silver is needed to be used as the protecting layer. Fig. 4 shows the EL spectra of the polymers. The EL spectra of PFNAP-5 and PFNAP-1 only exhibit yellowish-green emission $(\lambda_{max} = 545 \text{ nm})$ from M1 units. With the decrease of the M1 unit's content, the relative intensity of the band at $\lambda_{max}\,{=}\,430/460~nm$ increases because of the incomplete energy transfer from fluorene segments to M1 units. With the increase of the M1 unit's content, the vellowish-green emission band in the EL spectra of polymers is red-shifted when compared with that of other polymers because of the aggregation of M1 units at high M1 concentration. The aggregation of M1 units resulting from the interchain π - π interaction changes the HOMO and LUMO of the polymers, and reduces their bandgaps. That leads to the red-shifted emission band.

Table 3 shows the EL properties of polymers. The turn-on voltage, maximum brightness, and maximum luminous efficiency of polymers are: (7 V, 6534 cd/m², 0.56 cd/A) for PFNAP-5, (6 V, 13,300 cd/m², 1.1 cd/A) for PFNAP-1, (4.5 V, 26,200 cd/m², 1.49 cd/ A) for PFNAP-0.5, (4 V, 11,400 cd/m², 1.5 cd/A) for PFNAP-0.25, (4 V, 11,600 cd/m², 1.93 cd/A) for PFNAP-0.125, and (4 V, 6704 cd/m², 0.87 cd/A) for PFNAP-0.06, respectively. PFNAP-5 has a higher turnon voltage, a lower maximum brightness and a maximum luminous efficiency, which is due to the charge trapping effect and concentration quenching effect. The CIE coordinates of polymers are: (0.36, 0.56) for PFNAP-5, (0.36, 0.56) for PFNAP-1, (0.33, 0.54) for PFNAP-0.5, (0.32, 0.51) for PFNAP-0.25, (0.29, 0.47) for PFNAP-0.125, and (0.25, 0.34) for PFNAP-0.06. All the EL devices of polymers have good color stabilities. When M1 unit's content is 0.06 mol-%, the EL intensities of blue emission ($\lambda_{max} = 430/460 \text{ nm}$) and yellowishgreen emission ($\lambda_{max} = 510/530$ nm) are the same. Fig. 5 shows the EL spectra of the electroluminescent devices of PFNAP-0.06 under different bias conditions with corresponding CIE coordinates. At

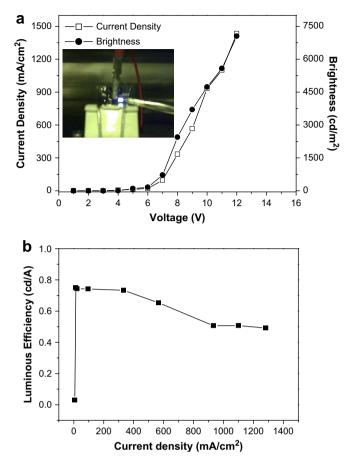


Fig. 8. The I–V–B curve (a) and the luminous efficiency (b) on different current densities of the white PLED system (PFNAP-0.06 blend with 1 mol-% Btplr).

different applied voltages, 8 V, 10 V, and 12 V, the CIE coordinates are (0.25, 0.33), (0.25, 0.34), and (0.25, 0.34), respectively. The current density (I)–voltage (V)–brightness (B) curves of the devices of polymers are shown in Fig. 6.

3.5. WPLED blending system (PFNAP-0.06 blended with 1 mol-% Btplr)

When PFNAP-0.06 is blended with 1 mol-% red phosphorescent iridium complex (BtpIr), we could balance the light colors and make a WPLED. At different applied voltages on the devices, the CIE coordinates and brightness of the WPLED device are 8 V [(0.34, 0.35), 2066 cd/m²], 9 V [(0.32, 0.34), 4030 cd/m²], 10 V [(0.31, 0.34), 4729 cd/m²], 11 V [(0.30, 0.36), 5578 cd/m²], and 12 V [(0.29, 0.37), 7050 cd/m²], respectively. The WPLED device exhibits blue emission ($\lambda_{max} = 430/460$ nm) from the fluorene segments, yellowishgreen emission ($\lambda_{max} = 510/530$ nm) from the M1 units, and red emission ($\lambda_{max} = 615/670$ nm) from the BtpIr. We could observe a pure white emission from the device during operation in the inset of Fig. 7. The EL spectra (Fig. 7) change slightly with applied voltages, and the red emission decreases with the increasing current density. This effect is due to a saturation of emission capability of iridium complex at higher current densities, which leads to change the CIE coordinates of EL spectra [36]. The overall performances of the WPLED devices are summarized in Table 3. Fig. 8 shows the typical current density (I)-voltage (V)-brightness (B) characteristic curve and current density-luminous efficiency curve of the electroluminescent device. Further improvement of the performance in the devices could be obtained by increasing the recombination of electrons and holes in the emission layer.

4. Conclusion

In summary, we have successfully developed a novel series of polymers by incorporation of M1 into polyfluorene by end-capping. The EL spectra of these polymers exhibit blue emission $\lambda_{max} = 430/$ 460 nm from the fluorene segments and yellowish-green emission $\lambda_{\text{max}} = 510/530 \text{ nm}$ from the M1 units due to the energy transfer and charge trapping from the fluorene segments to the M1 units. The relative intensities of the two emission bands can be tuned by adjusting the content of the M1 units. For the polymer with the M1 unit's content of 0.06 mol-%, the intensities of the blue emission and the yellowish-green emission in the EL spectrum are balanced. The device of PFNAP-0.06 emits blue and yellowish-green light with CIE coordinates of (0.25, 0.34), and exhibits a maximum brightness of 6704 cd/m² at 10 V. We have obtained a white-lightemitting device from a blue and yellowish-green emission polymer (PFNAP-0.06) blended with 1 mol-% BtpIr. The device emits white light with CIE coordinates of (0.32, 0.34) at 9 V, and exhibits a maximum brightness of 7050 cd/m^2 at 12 V. The approach is proved to be a useful way to prepare efficient WPLEDs.

Acknowledgments

The financial support provided by the National Science Council through project NSC-97-2627-E-006-001 is greatly appreciated. The authors also thank the Center for Micro/Nano Technology Research, National Cheng-Kung University, Tainan, Taiwan, for equipment access and technical support.

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