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Green polymer-light-emitting-diodes based on polyfluorenes containing N-aryl-1,8-naphthalimide and 1,8-naphthoilene-arylimidazole derivatives as color tuner

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ABSTRACT

A novel series of green light emitting single polymers were prepared by end-capping of N-aryl-1,8-naphthalimide and 1,8-naphthoilenearylimidazole derivatives into polyfluorene. The electroluminescence (EL) spectra of polymers (P1 ∼ P5) exhibit greenish-blue, bluish-green, pure green, and yellowish-green emission ($\lambda_{max} = 465$ nm, 490 nm, 500 nm, and 545 nm, respectively) from compounds (M1 ∼ M5). It was found that by the introduction of a small amount of compounds (M1 ∼ M5) (5 mol-%) into polyfluorene, the emission color can be tuned from the blue to green region. The color tuning was found to have gone through charge trapping and Förster energy transfer. The device of P4 emits pure green light with Commission Internationale de l'Eclairage (CIE) coordinates of (0.20, 0.41), and exhibits a maximum brightness of 11500 cd/m^2 at 12 V with a structure of indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene):poly(styrene sulfonic acid) [PEDOT:PSS]/PVK/emission layer/Ca/Ag. The device of P5 emits yellowish green light with Commission Internationale de l'Eclairage (CIE) coordinates of (0.36, 0.56), and exhibits a maximum brightness of 6534 cd/m^2 at 17 V.

1. Introduction

Recently, polymer-light-emitting diodes (PLEDs) have attracted considerable attention, because of their potential applications in back-lighting for liquid-crystal displays, full-color displays with a color filter, and lighting sources [1–7]. PLEDs can be processed by low cost solution-processing methods at room temperature, such as spin coating and inkjet printing [8,9]. Many studies obtain various materials and devices with high performance [10,11].

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 low-bandgap monomers into the polymer backbone [12–14]. PFs can be used as host materials to blend with other conjugated polymers, fluorescent dyes, and organometallic triplet emitters. Then, other colors can be generated through energy transfer from fluorene segments to lower-energy emitters [15–19].

On the other hand, N-aryl-1,8-naphthalimide derivatives having an electron-donating substituent on the 4-position are highly fluorescent [20–22]. Recently, many studies found that when N-aryl-1,8-naphthalimide derivatives were incorporated into a conjugated polymer, the resulting polymer could show great PL and EL efficiency [17,23,24]. If N–arylnaphthalimide and 1,8-naphthoilenearylimidazole derivatives have different electron withdrawing (or donating) groups and different coplanar degree of molecular structures, these groups can shift the photoluminescence (PL) wavelengths and change the quantum yields. Herein, we report the preparation and characterization of N-arylnaphthalimide and 1,8-naphthoilenearylimidazole derivatives (Scheme 1). By controlling the content of N-arylnaphthalimide and 1,8-naphthoilenearylimidazole derivatives, the emission color could be tuned from the blue (PFs) to green region (green dyes).

In our research, a novel series of green light emitting single polymers have been prepared by incorporation of N-arylnaphthalimide and 1,8-naphthoilenearyl-imidazole derivatives into polyfluorene by end-capping method. It was found that by the introduction of a small amount of compounds (5 mol-%) into polyfluorene, the emission color can be tuned from the blue to

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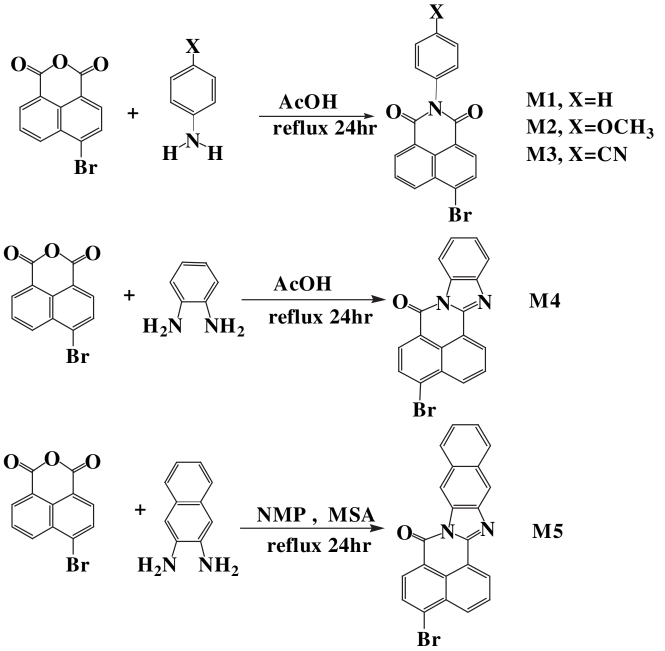


Scheme 1. Synthesis of compounds (M1 ~ M5).

green region. Energy transfer from fluorene segments to green dyes (M1 ~ M5) was observed. The green region emission band came from energy transfer and charge trapping from the fluorene segments to the green dyes (M1 ~ M5). We have achieved a new series type of green PLEDs from the PFs containing N-arylnaphthalimide and 1,8-naphthoilenearylimidazole derivatives.

2. Experimental

2.1. Instrumentation

The IR spectra were recorded on a Jasco 460 FTIR spectrometer. ^{1}H NMR spectra were collected on a Brucker Advance 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 (T_g) was determined on a TA Instruments Model 2920 Differential Scanning Calorimeter (DSC) at a heating rate of 20 °C/min under 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 tetra-n-butylammonium perchlorate $[CH_3(CH_2)_3]_4N\cdot ClO_4$ in acetonitrile.

2.2. Materials

2,7-Dibromo-9,9-dioctylfluorene, polyvinylcarbazole (PVK), 2,3-diaminonaph-thalene, o-phenylenediamine, 4-methoxyaniline, 4-aminobenzonitrile, aniline, 4-bromo-1,8-naphthalicanhydride, acetic acid, 2,2-dipyridyl, methanesulfonic acid (MSA), 1,5-cyclooctadiene, bis(1,5-cyclooctadiene)nickel (0) z[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, acetone and 1-methyl-2-pyrrolidinone (NMP) were also purchased from TEDIA.

2.3. Synthesis of compounds

2.3.1. Synthesis of 4-bromo-N-phenyl-1,8-naphthalimide (M1)

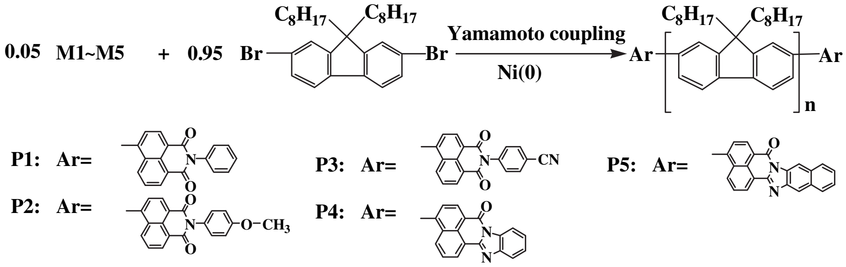
To a 100 mL round-bottom flask containing 1 g (3.6 mmol) of 4-bromo-1,8-naphthalic anhydride in 20 mL of acetic acid, 0.41 g (4.4 mmol) of aniline was added. The mixture was refluxed for 24 h. After reaction was complete, the mixture was poured into ice-water. The resulting precipitate was filtered and purified by recrystallization from acetone. A white powder M1 was obtained, and the yield was 76%; mp: 230 °C. FTIR: 1715, 1663, 1586, 1567 cm^{-1} (C═O), 964 cm^{-1} (–Br). ^{1}H NMR (600 MHz, CDCl$_3$, ppm): 7.32 (d, 2H), 7.55 (t,2H), 7.48 (t, 1H), 7.85 (t,1H), 8.09 (d, 1H), 8.43 (d, 1H), 8.60 (d, 1H), 8.68 (d, 1H). Elemental analysis (%) calcd: N, 3.98; C, 61.36; H, 2.84. Found (%): N, 3.88; C, 61.14; H, 2.90.

2.3.2. Synthesis of 4-bromo-N-(4-methoxyphenyl)-1,8-naphthalimide (M2)

The synthesis and purification were similar to M1. A white powder M2 was obtained, and the yield was 80%; mp: 240 °C. FTIR: 1718, 1668, 1586, 1570 cm^{-1} (C═O), 966 cm^{-1} (–Br). ^{1}H NMR (600 MHz, CDCl$_3$, ppm):3.87 (s, 3H), 7.07 (d, 2H), 7.24 (d, 2H), 7.87 (t, 1H), 8.07 (d, 1H), 8.45 (d, 1H), 8.62 (d, 1H), 8.69 (d, 1H). Elemental analysis (%) calcd: N, 3.66; C, 59.68; H, 3.14. Found (%): N, 3.59; C, 59.64; H, 3.25.

2.3.3. Synthesis of 4-bromo-N-(4-cyanoxyphenyl)-1,8-naphthalimide (M3)

The synthesis and purification were similar to M1. A pale yellow powder M3 was obtained, and the yield was 63%; mp: 240 °C. FTIR: 2225 cm^{-1} (C≡N), 1714, 1663, 1590, 1569 cm^{-1} (C═O), 970 cm^{-1} (–Br). ^{1}H NMR (600 MHz, CDCl$_3$, ppm): 7.66 (d, 2H), 8.03 (d, 2H),



Scheme 2. Synthesis of polymers.

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

Polymer	Mn(g/mol) × 10^4	Mw(g/mol) × 10^4	PDI[a]	T_g(°C)	T_{5d}(°C)[b]
P1	2.30	4.80	2.08	110	420
P2	1.20	2.90	2.41	112	424
P3	1.30	3.40	2.61	110	421
P4	1.66	2.77	1.66	113	417
P5	1.71	2.86	1.67	110	416

[a] Polydispersity.
[b] Temperature of 5% weight loss measured by TGA in nitrogen.

8.03 (t, 1H), 8.26 (d, 1H), 8.33 (d, 1H), 8.57 (d, 1H), 8.62 (d, 1H). Elemental analysis (%) calcd: N, 7.42; C, 60.50; H, 2.38. Found (%): N, 7.19; C, 60.51; H, 2.70.

2.3.4. Synthesis of 4-bromo-1,8-napthoilene-1,2-benzimidazole (M4)

The synthesis and purification were similar to M1. A bright yellow powder M4 was obtained, and the yield was 75%; mp: 277 °C. FTIR: 1696 cm^{-1} (C═O), 964 cm^{-1} (–Br). ^{1}H NMR (600 MHz, DMSO-d_6, ppm): 7.51 (d, 2H), 7.88 (d, 1H), 8.06 (t, 1H), 8.10 (t, 1H), 8.44 (d, 1H), 8.51–8.68 (m, 2H), 8.85 (d, 1H). Elemental analysis (%) calcd: N, 8.02; C, 61.89; H, 2.57. Found (%): N, 8.01; C, 61.77; H, 2.71.

2.3.5. Synthesis of 4-bromo-1,8-napthoilene-2,3-naphthalimidazole (M5)

To a 100 mL round-bottom 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. A bright orange powder M5 was obtained, and the yield was 85%; mp: 297 °C. FT IR: 1700 cm^{-1} (C═O), 971 cm^{-1} (–Br). ^{1}H NMR (600 MHz, DMSO-d_6, 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 2. All polymers were synthesized in the same way. The P1 is taken as 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 1.63 g (2.97 mmol) and M1 55 mg (0.156 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 82%. FT-IR: 1700 cm^{-1} (C═O). ^{1}H NMR (600 MHz, $CDCl_3$, ppm): 0.83 (broad), 1.2 (broad), 2.13 (broad), 7.5–7.9 (broad, Ar–H), 8.3–8.9 (broad, weak peaks of M1 units). Elemental analysis (%) Calcd: N, 0.18; C, 89.32; H, 10.07. Found (%): N, 0.14; C, 88.84; H, 10.07.

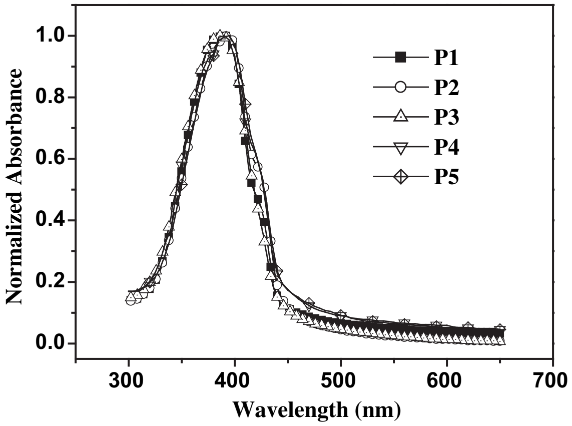


Fig. 1. UV–vis absorption spectra of the polymers in solid films.

2.4.1. Synthesis of P2

Reactants feed ratio: 2,7-dibromo-9,9-dioctylfluorene 1.63 g (2.97 mmol) and M2 60 mg (0.156 mmol). The yield was 78%. FT-IR: 1703 cm^{-1} (C═O). ^{1}H NMR (600 MHz, $CDCl_3$, ppm): 0.83 (broad),

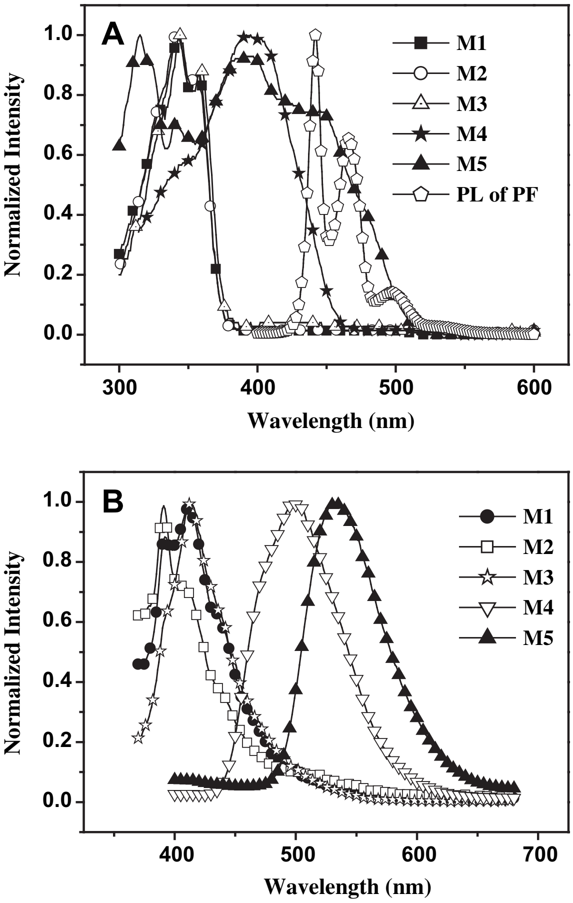


Fig. 2. Absorption spectrum of compounds (M1 ~ M5) dissolved in o-xylene and PL emission spectra of polyfluorene film (A). PL emission spectra of compounds (M1 ~ M5) dissolved in o-xylene (B).

Table 2
Optical properties and quantum yields of compounds (M1 ~ M5).

Compounds	UV–vis λ_{max} (nm)[a]	PL λ_{max} (nm)[a]	Quantum yield (Φ_F)[b]
M1	340/358	390/409	0.015
M2	340/358	390	0.010
M3	340/358	412	0.038
M4	349/392	500	0.820
M5	341/398/440	536	0.280

[a] Compounds were dissolved in o-xylene (10^{-5} M).

[b] Fluorescence quantum yields are relative to quinine sulfate ($\Phi_F = 0.55$) in water (10^{-5} M). Compounds were dissolved in o-xylene (10^{-5} M). Excitation wavelengths ranged between 330 nm and 360 nm.

Table 3
Electrochemical properties of copolymers.

Polymer	$E_{ox,onset}$	$E_{re,onset}$	$E_{ox,onset,\ vs\ FOC}$[b]	$E_{ox,onset,\ vs\ FOC}$[b]	HOMO[c]	LUMO[d]	Eg(eV)
PF[a]	1.36	−2.18	0.90	−2.64	−5.70	−2.16	3.54
P1	1.28	−2.20	0.82	−2.66	−5.62	−2.14	3.48
P2	1.33	−2.12	0.87	−2.58	−5.67	−2.12	3.45
P3	1.34	−2.15	0.88	−2.61	−5.68	−2.15	3.49
P4	1.33	−2.10	0.87	−2.56	−5.67	−2.24	3.43
P5	1.36	−1.98	0.90	−2.44	−5.70	−2.36	3.34

[a] PF: pure polyfluoroene (synthesized by our lab).

[b] $E_{FOC} = 0.46$ V vs Ag/Ag^+, FOC: Ferrocene.

[c] $E_{HOMO} = -e\ (E_{ox\ onset\ vs\ FOC} + 4.8\ V)$.

[d] $E_{LUMO} = -e\ (E_{red\ onset\ vs\ FOC} + 4.8\ V)$.

1.2 (broad), 2.13 (broad), 7.5–7.9 (broad, Ar–H), 8.3–8.9 (broad, weak peaks of M2 units). Elemental analysis (%) Calcd: N, 0.18; C, 89.13; H, 10.06. Found (%): N, 0.15; C, 88.51; H, 10.08.

2.4.2. *Synthesis of P3*

Reactants feed ratio: 2,7-dibromo-9,9-dioctylfluorene 1.63 g (2.97 mmol) and M3 58 mg (0.156 mmol). The yield was 84%. FT-IR: 1697 cm^{-1} (C=O). ^1H NMR (600 MHz, $CDCl_3$, ppm): 0.83 (broad), 1.2 (broad), 2.13 (broad), 7.5–7.9 (broad, Ar–H), 8.3–8.9 (broad, weak peaks of M3 units). Elemental analysis (%) Calcd: N, 0.36; C, 89.20; H, 10.01. Found (%): N, 0.29; C, 88.77; H, 10.11.

2.4.3. *Synthesis of P4*

Reactants feed ratio: 2,7-dibromo-9,9-dioctylfluorene 1.1 g (2.04 mmol) and M4 37 mg (0.106 mmol). The yield was 76%. FT-IR: 1699 cm^{-1} (C=O). ^1H NMR (600 MHz, $CDCl_3$, ppm): 0.83 (broad), 1.2 (broad), 2.13 (broad), 7.5–7.9 (broad, Ar–H), 8.3–8.9 (broad, weak peaks of M4 units). Elemental analysis (%) Calcd: N, 0.37; C, 89.36; H, 10.06. Found (%): N, 0.32; C, 89.37; H, 10.13.

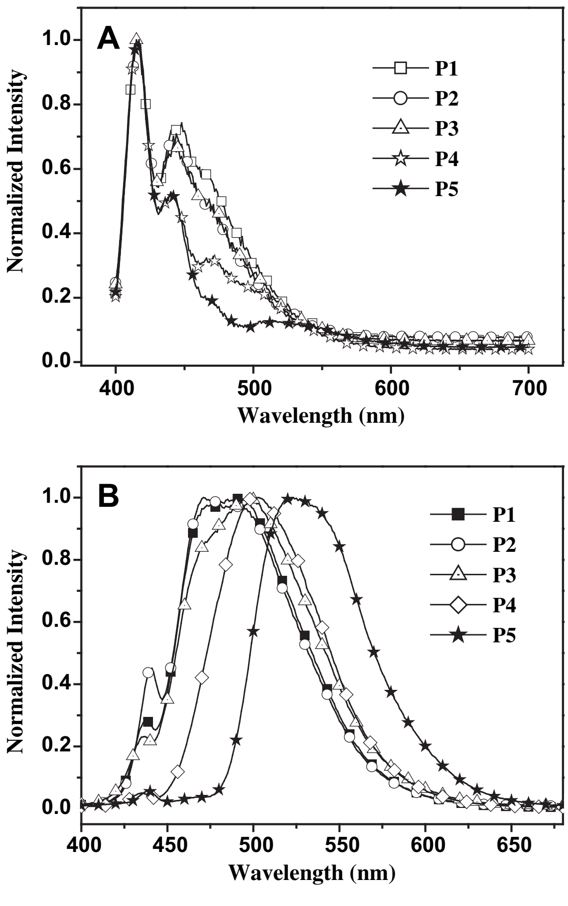


Fig. 3. PL emission spectra of the polymers in dilute solution (in o-xylene) (A) and solid films (B).

2.4.4. *Synthesis of P5*

Reactants feed ratio: 2,7-dibromo-9,9-dioctylfluorene 1.51 g (2.75 mmol) and M1 58 mg (0.145 mmol). The yield was 80%. FT-IR: 1700 cm^{-1} (C=O). ^1H NMR (600 MHz, $CDCl_3$, ppm): 0.83 (broad), 1.2 (broad), 2.13 (broad), 7.5–7.9 (broad, Ar–H), 8.3–8.9 (broad, weak peaks of M5 units). Elemental analysis (%) calcd: N, 0.36; C, 89.53; H, 10.03; Found (%): N, 0.30; C, 89.21; H, 10.01.

2.5. *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 spin-coated onto 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 a glass Petri dish overnight. On top of the sample, 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 thermo-evaporation 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

3.1. *Synthesis and characterization of the polymers*

Compounds (M1 ~ M5) were synthesized from the condensation reaction of 4-bromo-1,8-naphthalic anhydride and aniline derivatives (aniline, 4-methoxyaniline, 4-aminobenzonitrile, o-phenylenediamine, 2,3-diaminonaphthalene). Compounds (M1 ~ M5) were easy to synthesize and purify by recrystallization. The yield of the reactions ranged from 63% to 85%. The polymerization reactions were carried out via a Yamamoto polycondensation reaction with Ni(0) as the catalyst. Compounds (M1 ~ M5) were introduced to the polymers by end-capping. The amount of compounds (M1 ~ M5) added to the polymerization were 5 mol-% (Scheme 2). The yield of the polymerization reactions ranged from 76% to 84%. The end-capping reaction could decrease the molecular weight of polymers. In our research, the

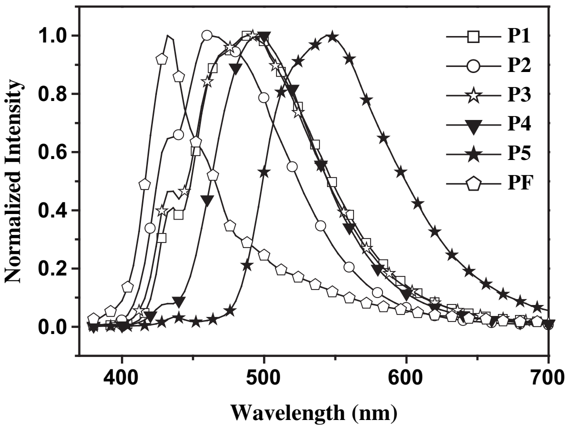


Fig. 4. EL spectra of the electroluminescent devices of the polymers (P1 ∼ P5 and polyfluorene).

weight-average molecular weight (M_w) of pure polyfluorene is about 60000 g/mol, but the weight-average molecular weights (Mw) of these end-capping polymers are from 27700 g/mol to 48000 g/mol, and the number-average molecular weights (M_n) are from 12000 g/mol to 23000 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 ^{1}H NMR and elemental analysis. The signal at 8.3–8.9 ppm in ^{1}H NMR spectra and the N contents from elemental analysis are attributed to the compounds (M1 ∼ M5), and the actual contents of the compounds (M1 ∼ M5) in the polymers could be calculated. The actual contents of compounds (M1 ∼ M5) in polymers (P1 ∼ P5) are 4 mol-%, 4.16 mol-%, 4.02 mol-%, 4.32 mol-%, and 4.2 mol-%, respectively. The actual contents of compounds (M1 ∼ M5) are close to the feed ratio in the polymerization.

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 416 to 424 °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 110–113 °C (Table 1). All polymers have higher T_gs than pure polyfluorene ($T_g = 76\ ^\circ$C), which is due to the compounds (M1 ∼ M5) having a rigid molecular structure. The rigid molecular structure limits the motion of polymer chains.

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 compounds (M1 ∼ M5) could not be observed from the spectra, because their content in the polymer chain is quite low.

Fig. 2(A) shows the UV/vis absorption spectra of compounds (M1 ∼ M5) in o-xylene and the PL emission spectrum of polyfluorene film. The absorption peaks of M1 ∼ M5 are summarized in Table 2. Energy transfer from the fluorene segments to the vicinity of M4 and M5 units were better than M1, M2, and M3 (Fig. 3(B)). Fig. 3(B) shows the PL spectra of the polymer films. The PL peak of the fluorene unit (437 nm) of P4 and P5 almost disappear. It is due to greater overlapping of the PL spectrum of polyfluorene and UV/vis spectra of M4 and M5 (Fig. 2(A)).

Table 4
EL properties of polymers.

Polymer	Brightness max (cd/m^2)	Turn-on voltage (V)	Luminous efficiency max (cd/A)	EL λ_{max} (nm)	CIE (x,y)
P1	930	11	0.19	433/490	(0.20,0.33) Bluish green
P2	2890	10	0.28	433/465	(0.17,0.22) Greenish blue
P3	772	11	0.15	433/490	(0.20,0.31) Bluish green
P4	11500	6	0.83	500	(0.20,0.41) Green
P5	6534	7	0.56	545	(0.36,0.56) Yellowish green

Fig. 2(B) shows the PL emission spectra of compounds (M1 ∼ M5). The PL peaks and quantum yields of M1 ∼ M5 are summarized in Table 2. Fluorescence quantum yields are relative to quinine sulfate ($\Phi_F = 0.55$) in water (10^{-5} M). Compounds (M1 ∼ M5) were dissolved in o-xylene (10^{-5} M). Excitation wavelengths ranged between 330 nm and 360 nm. Compounds (M1 ∼ M5) are dyes with different electron withdrawing (or donating) groups and different coplanar degree of molecular structures. These groups can shift the photoluminescence (PL) wavelengths and change the quantum yields.

Fig. 3 shows the PL spectra of the polymers in dilute o-xylene solution and in thin solid films with the excitation at 380 nm. The PL spectra of these polymers in dilute o-xylene (Fig. 3(A)) show two emission bands. The band in the blue region (400–460 nm) is attributed to the fluorene segments, and the other band in the green region (460–540 nm) is due to the emission from the vicinity of the compounds (M1 ∼ M5). The green emission band could come from the Förster energy transfer from fluorene segments to the compounds (M1 ∼ M5) [25].

The PL spectra of these polymers in solid film (Fig. 3(B)) show green emission bands. It is due to the more complete energy transfer from the fluorene segments to the vicinity of the compounds (M1 ∼ M5) in solid film. In a dilute solution, polymer chains are separated by solvent molecules, and intrachain energy transfer is the major mechanism (Fig. 3(A)). In a solid film, polymer chains are packed together, enabling both intrachain energy transfer and interchain energy transfer (Fig. 3(B)) [26].

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. According to the formula, $E_{FOC} = 0.46$ 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 −5.62 eV to −5.70 eV and −2.12 eV to −2.36 eV, respectively (Table 3). The results show that the energy levels of the polymers have slight changes than that of pure polyfluorene [27].

3.4. Electroluminescence (EL) properties of the devices

The devices were fabricated in the configuration of ITO/PEDOT:PSS/PVK/emission layer/Ca/Ag. Fig. 4 shows the EL spectra of the polymers. The EL spectra of polymers exhibit greenish-blue, bluish-green, pure green, and yellowish-green emission ($\lambda_{max} = 465$ nm, 490 nm, 500 nm, and 545 nm, respectively) from compounds (M1 ∼ M5) (Table 4). It was found that by the introduction of a small amount of compounds (5 mol-%) into

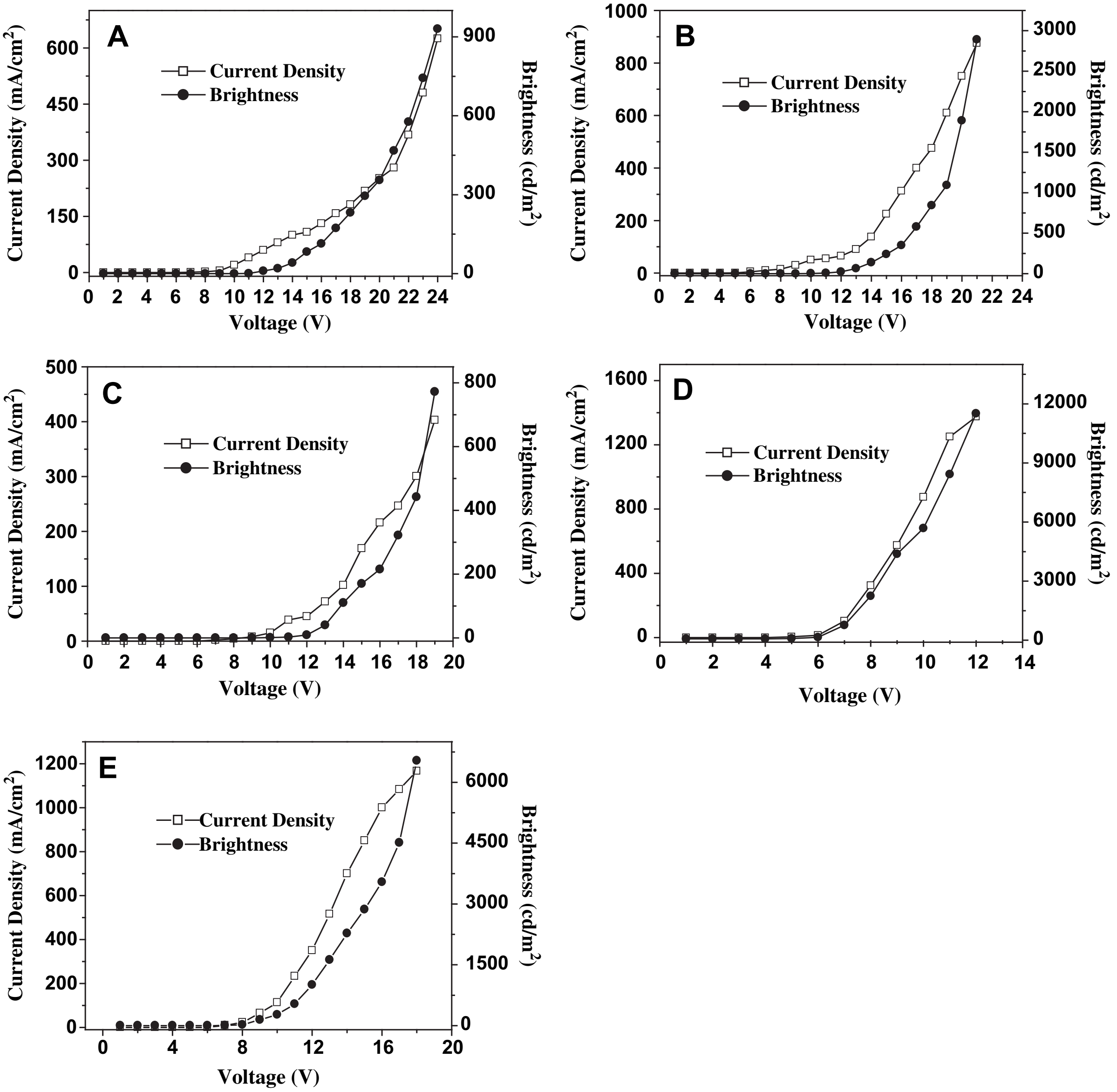


Fig. 5. I-V-B curves of polymers: (A) P1, (B) P2, (C) P3, (D) P4, and (E) P5.

polyfluorene, the emission color can be tuned from the blue to green region. The color tuning was found to go through charge trapping and Förster energy transfer. Electrons and holes are trapped in the compounds (M1 ~ M5) with two modes. One is that the holes and electrons from respective electrodes are directly trapped by the compounds (M1 ~ M5), leading to compounds (M1 ~ M5) emission. Another is that the holes and electrons are initially injected and transported along fluorene segments. Then the electrons and holes are trapped by the compounds (M1 ~ M5). The EL spectra of P1, P2, and P3 also exhibit a blue peak of fluorene ($\lambda_{max} = 433$ nm), because of the incomplete energy transfer from fluorene segments to M1, M2, and M3 units.

Table 4 shows the EL properties of polymers. The turn-on voltage, maximum brightness, and maximum luminous efficiency of polymers are: (11 V, 930 cd/m^2, 0.19 cd/A) for P1, (10 V, 2890 cd/m^2, 0.28 cd/A) for P2, (11 V, 772 cd/m^2, 0.15 cd/A) for P3, (6 V, 11500 cd/m^2, 0.83 cd/A) for P4, and (7 V, 6534 cd/m^2, 0.56 cd/A) for P5, respectively. P1, P2, and P3 have higher turn-on voltages and lower current density (Fig. 5), because the polarity of N-aryl-1,8-naphthalimide derivatives (M1, M2, and M3) is higher than 1,8-naphthoilenearylimidazole derivatives (M4 and M5), which creates a greater charge trapping effect than P4 and P5.

The CIE coordinates of polymers are: (0.20, 0.33) for P1, (0.17, 0.22) for P2, (0.20, 0.31) for P3, (0.20, 0.41) for P4, and (0.36, 0.56) for P5, respectively. All the EL devices of polymers have good color stabilities. The current density (I)–voltage (V)–brightness (B) curves of the devices of polymers are shown in Fig. 5.

4. Conclusion

In summary, we have successfully developed a novel series of polymers by the incorporation of compounds (M1 ~ M5) into polyfluorene by end-capping. The EL spectra of these polymers exhibit greenish blue emission ($\lambda_{max} = 465$ nm) from P2, bluish green emission ($\lambda_{max} = 490$ nm) from P1 and P3, pure green emission ($\lambda_{max} = 500$ nm) from P4, and yellowish-green emission ($\lambda_{max} = 545$ nm) from P5 due to the energy transfer and charge trapping from the fluorene segments to the compounds

(M1 ~ M5). Green emission compounds (M1 ~ M5) were easy to synthesize and purify by recrystallization. The yield of the condensation reactions ranged from 63% to 85%.

The device of P4 emits pure green light with CIE coordinates of (0.20, 0.41), and exhibits a maximum brightness of 11500 cd/m^2 at 12 V. We have obtained a green-light-emitting device from polyfluorene containing green dyes. This approach has proved to be a useful way to prepare efficient green emission PLEDs.

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