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Green electroluminescent polyfluorenes containing 1,8-naphthalimide moieties as color tuner

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Dedicated to the memory of Professor Baotong Huang on the first anniversary of his death.

Abstract

A series of copolymers (CNPFs) containing low-band-gap 1,8-naphthalimide moieties as color tuner was prepared by a Yamamoto coupling reaction of 2,7-dibromo-9,9-dioctylfluorene (DBF) and different amount of 4-(3,6-dibromocarbazol-9-yl)-*N*-(4′-*tert*-butyl-phenyl)-1,8-naphthalimide (Br–CN) (0.05–1 mol% feed ratio). The light emitting properties of the resulting copolymers showed a heavy dependence on the feed ratio. In photoluminescence (PL) studies, an efficient color tuning through the Förster energy transfer mechanism was revealed from blue to green as the increase of Br–CN content, while in electroluminescence (EL) studies, the color tuning was found to go through a charge trapping mechanism. It was found that by introduction of a very small amount of Br–CN (0.1–0.5 mol%) into polyfluorene, the emission color can be tuned from blue to pure green with Commission International de l'Echairage (CIE) coordinates being (0.21, 0.42) and (0.21, 0.48). A green emitting EL single-layer device based on CNPF containing 0.1 mol% of Br–CN showed good performances with a low turn-on voltage of 4.2 V, a brightness of 9104 cd/m^2, the maximum luminous efficiency of 2.74 cd/A and the maximum power efficiency of 1.51 lm/W. To further improve the EL performances through balancing the charge trapping process, a copolymer (BCNPF05) derived from 0.5 mol% of a triarylamine-containing 4-{3,6-bis-[4″-(4‴-bromophenyl-*p*-tolyl-amino)-phenyl]-carbazol-9-yl}-*N*-(4′-*tert*-butyl-phenyl)-1,8-naphthalimide (Br–BCN) and 99.5 mol% of 2,7-dibromo-9,9-dioctylfluorene was also prepared. As expected, a single layer EL device based on BCNPF05 exhibited better performances with a brightness of 14228 cd/m^2, the maximum luminous efficiency of 4.53 cd/A and the maximum power efficiency of 1.57 lm/W.

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1. Introduction

Organic polymers are potential candidates for light emitting diode (LED) applications. In comparison with inorganic and small molecular organic light-emitting materials, organic polymers appear to be more advantageous in terms of lower production costs, high flexibility, readily processability and the possibility of uniformly covering large areas by inexpensive solution processing techniques [1]. Up to now, a wide variety of fluorescent conjugated polymers [2–12] has been developed for LED applications and some structure–property relationships have been established. However, critical issues in the development of polymeric LED (PLED) for practice device applications remain to be resolved, which include the optimization of device performances and improvement of cost effectiveness. To address these issues, innovations are being actively pursued to achieve novel light-emitting polymers, which are easy to be prepared in large scale, have excellent processability and optical performances such as well-defined emission color, narrow bandwidth, low birefringence, and good chemical and physical stability.

Polyfluorenes (PFs) are well known blue-emitting materials and have high luminescence efficiency, excellent thermal and oxidative stability and good processability [8,13–18]. Structural modification of PFs represents an attractive approach to

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producing efficient PLED materials. Recently, introduction of a small amount of low-band-gap moieties (e.g. <5 mol%) into PF has been demonstrated as an efficient approach to tuning the emission color. For example, Müllen et al. [19] introduced perylenes into PF and obtained polymers with emission color adjustable throughout the whole visible range. Shim et al. [20] co-polymerized a small fraction (1.4%) of a thiophene derivative, i.e. 2,5-bis(2-(5′-bromothienyl)-1-cyanovinyl)-1-(2″-ethylhexyl)-4-methoxybenzene (BTCVB), with fluorene and the resulting copolymer exhibited a 115 nm red-shift in both the photoluminescence (PL) and electroluminescence (EL). Jen et al. [21] successfully synthesized a green emitting polymer by introducing benzothiadiazole moieties into the PF structure. A double-layer device based on such a polymer exhibited a low turn-on voltage (3.4 V) and very high external quantum efficiency (6.0%).

On the other hand, 1,8-naphthalimides having an electron-donating substituent on the 4-position are highly fluorescent and have found applications in a variety of fields such as brightening agents and laser dyes [22–24]. Although endeavor [25–29] has been made to explore their potential use in PLED by incorporating 1,8-naphthalimides into non-conjugated polymers, little progress has been achieved due to low luminescence efficiency. Recently, studies in our group found that when 1,8-naphthalimides were incorporated into a conjugated polymer, the resulting polymer could show a great enhancement in both PL and EL efficiency [30,31]. Furthermore, by changing the electron-donating property of the substituent at the 4-position of 1,8-naphthalimide, the emission color of the resulting polymer was tunable within a large range. Given these results and considering that polymers with pure emission colors (i.e. red, green and blue) and narrow bandwidth are highly desired for a full color flat-panel display, it was believed meaningful to study 1,8-naphthalimide-containing conjugated polymers as potential PLED materials. A careful molecular engineering of such a polymer may yield materials whose emission colors are well defined and tunable within the whole visible range.

Herein, we report the preparation and characterization of a series of green-emitting, 1,8-naphthalimide-containing PFs. By controlling the content of 1,8-naphthalimide, the emission color could be fine-tuned from blue to green. The color tuning mechanisms in PL and EL were studied and EL devices based on the resulting polymers were fabricated and showed high performances.

2. Experimental section

2.1. Measurements

^{1}H NMR spectra were recorded on a Bruker Avance 300 MHz NMR spectrometer. The chemical shifts relative to tetramethylsilane as internal reference are reported in the parts per million scale. The UV–vis spectrum was recorded on a Perkin–Elmer Lambda 35 UV–vis spectrometer. Molecular weights and polydispersity of polymers were determined by gel permeation chromatography (GPC) analysis with a Waters 410 instrument relative to polystyrene standards in tetrahydrofuran (THF) solution. Differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) were performed using Perkin–Elmer-DSC7 under the nitrogen atmosphere at a heating rate of 20 °C min^{-1}. Photoluminescent and electroluminescent spectrum were measured by Perkin–Elmer LS50B spectrofluorometer. Cyclic voltammograms of polymer films and small molecular model compound were recorded on an EG&G 283 (Princeton Applied Research) at room temperature in a solution of tetrabutylammonium perchlorate (n-Bu$_4$NClO$_4$) (0.10 M) in either acetonitrile or dichloromethane at a scan rate of 100 mV/s. A Pt wire was used as the counter electrode and a Ag/Ag$^+$ electrode as the reference electrode. For the measurement of EL, a polymer LED was constructed as follows: ITO-coated glass substrates were first thoroughly cleaned in an ultrasonic solvent bath and then dried in a heating chamber at 120 °C. Poly(styrene sulfonic acid)–doped poly(ethylenedioxythiophene) (PEDOT-PSS) was spin-coated on the ITO glasses at a speed of 3000 rps for 60 s and then baked for 15 min at 120 °C to give a thin layer film of about 50 nm thick. The light-emitting polymer layer was then deposited onto the film by spin-coating a polymer solution in chloroform (10 mg/mL) at a speed of 1500 rps for 60 s. Uniform and pinhole-free films with thicknesses around 100 nm could be readily obtained. Finally, a thin layer of calcium (about 10 nm) and a layer of aluminum (about 100 nm) were deposited in sequence in a vacuum (10^{-6} Torr) thermal evaporator through a shadow mask, yielding active areas of 16 mm^2. For device characterizations, current–voltage–brightness (I–V–B) was measured using a Keithley 2400/2000 current/voltage source unit with a calibrated silicon photodiode. All the above processes and measurements were carried out in the open air and at room temperature.

2.2. Materials

All the reagents and solvents used in this study were purchased from Aldrich and Acros companies and were used without further purification except for toluene that was dried over sodium/benzophenone and distilled. The monomer 2,7-dibromo-9,9′-dioctyl-fluorene was synthesized according to literature method [32].

2.2.1. N-(4′-tert-Butyl-phenyl)-4-bromo-1,8-naphthalimide (BN)

A mixture of 4-bromo-1,8-naphthalic anhydride (8.00 g, 28.9 mmol) and 4-*tert*-butyl-phenylamine (4.53 g, 30.4 mmol) in acetic acid (100 ml) was refluxed overnight. After cooling, the mixture solution was poured into distilled water (300 ml). The resultant gray solid was collected by filtration and then recrystallized from acetone to afford pure BN (7.07 g, 59.9%). ^{1}H NMR (CDCl$_3$): δ 8.68 (d, 1H), 8.59 (d, 1H), 8.43 (d, 1H), 8.04 (d, 1H), 7.86 (t, 1H), 7.56 (d, 2H), 7.23 (d, 2H), 1.40 (s, 9H).

2.2.2. 4-(Carbazol-9-yl)-N-(4′-tert-butyl-phenyl)-1,8-naphthalimide (CN)

A mixture of BN (4.00 g, 9.80 mmol), carbazole (2.20 g, 13.16 mmol), K_2CO_3 (2.40 g, 17.39 mmol), CuI (0.20 g, 1.05 mmol) and 18-crown-6 (0.20 g, 0.76 mmol) was heated at 180 °C under nitrogen for 12 h. After the mixture was cooled to room temperature, $CHCl_3$ (100 ml) and water (50 ml) were added, and the organic layer was separated and washed with distilled water three times. The $CHCl_3$ solution was concentrated by rotary-evaporator and the residue was subjected to a column chromatography using hexane/chloroform (3:1, v/v) as the eluent to yield CN (1.52 g, 31.4%). ^{1}H NMR ($CDCl_3$): δ 8.85 (d, 1H), 8.70 (d, 1H), 8.45 (d, 1H), 7.57–7.50 (m, 3H), 7.40 (d, 1H), 7.30–7.22 (d, 6H), 7.00 (m, 4H), 1.38 (s, 9H). Anal. Calcd for $C_{34}H_{26}N_2O_2$: C, 82.57; H, 5.30; N, 5.66. Found: C, 82.22; H, 5.71; N, 5.60. FD-MS: *m/z* 494.1 [M$^+$](100%).

2.2.3. 4-(3,6-Dibromocarbazol-9-yl)-N-(4′-tert-butyl-phenyl)-1,8-naphthalimide (Br–CN)

To a solution of CN (1.30 g, 2.63 mmol) in $CHCl_3$ (30 ml) was added Bu_4NBr_3 in portions in 10 min at room temperature. After stirred for 12 h, the resulting solution was washed with saturated aqueous Na_2SO_3 followed by distilled water twice. The organic solution was dried over anhydrous magnesium sulfate, concentrated by rotary-evaporator and subjected to a column chromatography using hexane/chloroform (3:1, v/v) as the eluent to yield Br–CN (1.52 g, 88.9%). ^{1}H NMR ($CDCl_3$): δ 8.85 (d, 1H), 8.72 (d, 1H), 8.28 (d, 1H), 7.91 (d, 1H), 7.68 (m, 2H), 7.60 (m, 2H), 7.50 (d, 2H), 7.25 (d, 1H), 6.90 (d, 2H), 1.38 (s, 9H). Anal. Calcd for $C_{34}H_{24}Br_2N_2O_2$: C, 62.60; H, 3.71; N, 4.29. Found: C, 62.13; H, 3.58; N, 4.21. FD-MS: *m/z* 649.8 [M+](100%).

2.2.4. 4-{3,6-Bis-[4″-(phenyl-p-tolyl-amino)-phenyl]-carbazol-9-yl}-N-(4′-tert-butyl-phenyl)-1,8-naphthalimide (BCN)

To a round-bottomed flask, were charged phenyl-[4-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-phenyl]-*p*-tolyl-amine (1.40 g, 3.65 mmol), Br–CN (1.05 g, 1.61 mmol), sodium carbonate (2.50 g, 18.1 mmol), $Pd(PPh_3)_4$ (0.02 g, 0.02 mmol), 15 ml of degassed toluene and 10 ml of water. The mixture was stirred at 80 °C under argon for 48 h, cooled to room temperature and then was poured into chloroform (100 ml). The organic layer was separated by a separatory funnel, washed with distilled water three times and then dried over anhydrous sodium sulfate. After column chromatography using hexane/chloroform (1:1, v/v) as the eluent, orange-red power was obtained (1.28 g, 78.8% yield). ^{1}H NMR ($CDCl_3$): δ 8.86 (d, 1H), 8.73 (d, 1H), 8.42 (s, 2H), 8.04 (d, 1H), 7.92 (t, 1H), 7.71 (t, 2H), 7.60 (m, 8H), 7.28–7.39 (m, 7H), 6.82–7.20 (m, 18H), 1.56 (s, 6H), 1.40 (s, 9H). Anal. Calcd for $C_{72}H_{56}N_4O_2$: C, 85.69; H, 5.59; N, 5.55. Found: C, 85.12; H, 5.51; N, 5.62. FD-MS: *m/z* 1008.4 [M$^+$](100%).

2.2.5. 4-{3,6-Bis-[4″-(4‴-bromophenyl-p-tolyl-amino)-phenyl]-carbazol-9-yl}-N-(4′-tert-butyl-phenyl)-1,8-naphthalimide (Br–BCN)

To a solution of BCN (0.38 g, 0.38 mmol) in $CHCl_3$ (30 ml) was added Bu_4NBr_3 (0.45 g, 0.93 mmol) in portions in 10 min. After stirred for 12 h, the resulting solution was washed with saturated aqueous Na_2SO_3 followed by distilled water. The organic phase was isolated, concentrated by rotary-evaporator, and then subjected to a column chromatography using hexane/chloroform mixture (1:1, v/v) as the eluent to yield Br–BCN (0.35 g, 78.9%). ^{1}H NMR ($CDCl_3$): δ 8.86 (d, 1H), 8.73 (d, 1H), 8.42 (s, 2H), 8.04 (d, 1H), 7.92 (t, 1H), 7.71 (t, 2H), 7.60 (m, 8H), 7.28–7.39 (m, 7H), 6.82–7.20 (m, 16H), 1.56 (s, 6H), 1.40 (s, 9H). Anal. Calcd for $C_{72}H_{54}Br_2N_4O_2$: C, 74.10; H, 4.66; N, 4.80. Found: C, 73.82; H, 4.51; N, 4.68. FD-MS: *m/z* 1164.3 [M$^+$](100%).

2.3. Polymerization

Both the homo-polymerization of 2,7-dibromo-9,9-dioctylfluorene (DBF) and the co-polymerization of DBF with Br–CN or Br–BCN were carried out through a nickel(0)-mediated Yamamoto coupling reaction [33]. The feed ratio of Br–CN were varied during co-polymerization from 0.05 to 1.0 mol%, in relative to the total amount of monomers, to adjust the CN content in the polymer. For the copolymer BCNPF05 that was derived from DBF and Br–BCN, the feed ratio of Br–BCN was fixed to 0.5 mol%.

2.3.1. Polyfluorene (PF)

A tub containing bis(1,5-cyclooctadiene)nickel(0) ($Ni(COD)_2$) (0.62 g, 2.2 mmol), α,α'-dipyridyl (Bpy) (0.25 g, 2.2 mmol), 1,5-cyclooctadiene (COD) (0.35 g, 2.2 mmol) and DMF (5 ml) was kept under argon at 80 °C for 20 min, and then a solution of 2,7-dibromo-9,9-dioctylfluorene (0.5484 g, 1.000 mmol) in toluene (5 ml) was added. The tub was closed and the polymerization was allowed to proceed at 80 °C for 4 days. After the reaction was finished, the polymer was precipitated from an equi-volume mixture (300 ml) of concentrated HCl aqueous, methanol and acetone. The isolated polymer was dissolved in $CHCl_3$ (300 ml), washed with 0.5 M aqueous HCl (200 ml), and then H_2O until neutral. The concentrated organic layer was precipitated in methanol and the resulting polymer product was further purified by extraction with acetone in a Soxhlet apparatus to remove small molecular away, dissolved in $CHCl_3$, precipitated in methanol again, and then dried in vacuum at room temperature to yield white fibers (0.2902 g, 74.7%).

2.3.2. Copolymers. The synthetic procedure for copolymers is illustrated with the typical synthesis of CNPF005

A tub containing bis(1,5-cyclooctadiene)nickel(0) ($Ni(COD)_2$) (0.62 g, 2.2 mmol), α,α'-dipyridyl (Bpy) (0.25 g, 2.2 mmol), 1,5-cyclooctadiene (COD) (0.35 g, 2.2 mmol), DMF (5 ml) was kept under argon at 80 °C for 20 min, and then a solution of 2,7-dibromo-9,9-dioctylfluorene (0.5481 g, 0.9995 mmol) and Br–CN (0.0003 g, 0.0005 mmol) in toluene

(5 ml) was added. The tub was closed and the polymerization was maintained at 80 °C for 4 days. After the reaction was finished, the polymer was precipitated from an equi-volume mixture (300 ml) of concentrated HCl aqueous, methanol and acetone. The isolated polymer was dissolved in $CHCl_3$ (300 ml), washed with 0.5 M aqueous HCl (200 ml), and then H_2O, until neutral. The concentrated organic layer was precipitated in methanol and the resulting polymer product was further purified by extraction with acetone in a Soxhlet apparatus to remove small molecular away, dissolved in $CHCl_3$, precipitated in methanol again, and then dried in vacuum at room temperature to yield light-yellow fibers (0.2796 g, 71.9% yield). IR (KBr, cm^{-1}): 3018 (m), 2954 (s), 2929 (s), 2854 (s), 1892 (w), 1778 (w), 1611 (w), 1458 (s), 1402 (m), 1377 (m), 1253 (m), 1136 (w), 999 (m), 885 (m), 813 (m), 758 (m), 722 (m).

2.3.3. CNPF01

2,7-Dibromo-9,9-dioctylfluorene (0.5479 g, 0.9990 mmol) and Br–CN (0.0007 g, 0.0011 mmol) were used in polymerization (0.2760 g, 71.0% yield). IR (KBr, cm^{-1}): 3020 (m), 2956 (s), 2929 (s), 2856 (s), 1892 (w), 1778 (w), 1716 (vw, very weak, carbonyl in 1,8-naphthalimide unit), 1678 (vw, carbonyl in 1,8-naphthalimide unit), 1612 (w), 1460 (s), 1405 (m), 1379 (m), 1255 (m), 1138 (w), 1001 (m), 887 (m), 815 (m), 760 (m), 724 (m).

2.3.4. CNPF05

2,7-Dibromo-9,9-dioctylfluorene (0.5457 g, 0.9950 mmol) and Br–CN (0.0033 g, 0.0051 mmol) were used in polymerization (0.2745 g, 70.6% yield). IR (KBr, cm^{-1}): 3006 (m), 2954 (s), 2927 (s), 2854 (s), 1889 (w), 1775 (w), 1716 (w, carbonyl in 1,8-naphthalimide unit), 1678 (w, carbonyl in 1,8-naphthalimide unit), 1610 (w), 1458 (s), 1403 (m), 1377 (m), 1254 (m), 1135 (w), 1000 (m), 885 (m), 813 (m), 757 (m), 722 (m).

2.3.5. CNPF1

2,7-Dibromo-9,9-dioctylfluorene (0.5430 g, 0.9901 mmol) and Br–CN (0.0065 g, 0.0100 mmol) were used in polymerization (0.2782 g, 71.4% yield). IR (KBr, cm^{-1}): 3007 (m), 2954 (s), 2927 (s), 2854 (s), 1889 (w), 1779 (w), 1716 (w, carbonyl in 1,8-naphthalimide unit), 1678 (w, carbonyl in 1,8-naphthalimide unit), 1610 (w), 1458 (s), 1403 (m), 1377 (m), 1254 (m), 1135 (w), 1000 (m), 885 (m), 813 (m), 757 (m), 722 (m).

2.3.6. BCNPF05

2,7-Dibromo-9,9-dioctylfluorene (0.5457 g, 0.9950 mmol) and Br–BCN (0.0058 g, 0.0050 mmol) were used in polymerization (0.2802 g, 71.9% yield).

3. Results and discussion

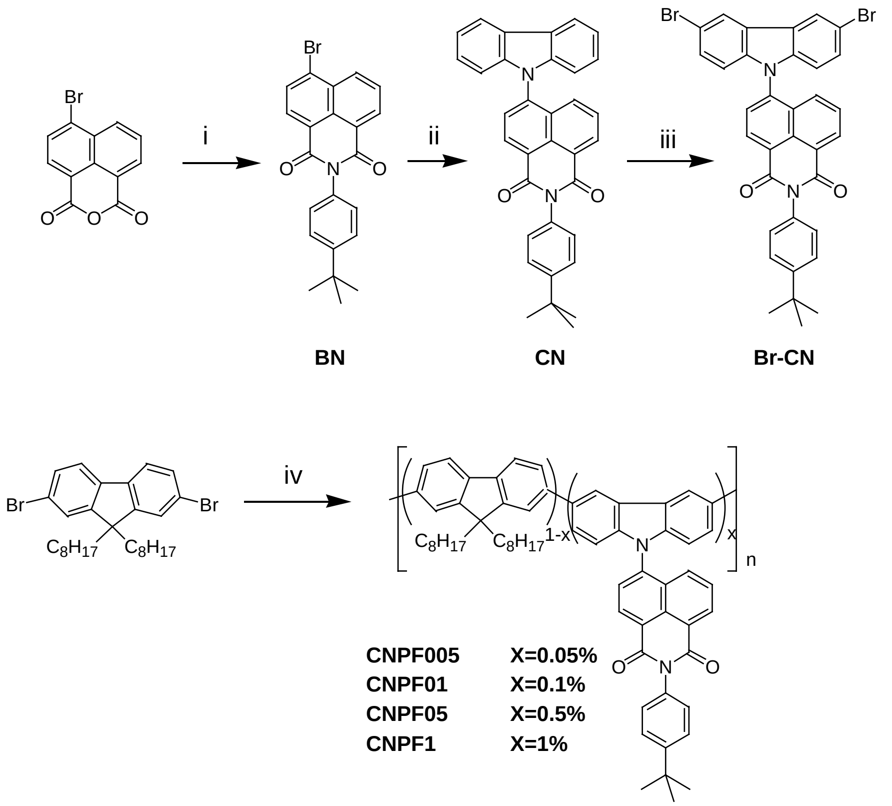
3.1. Synthesis

1,8-Naphthalimide derivatives having electron-donating substituents at the 4-position are highly fluorescent compounds. Although effort in developing 1,8-naphthalimide-containing side-chain non-conjugated polymers as potential candidates for PLED applications did not make much progress due to a low light-emitting efficiency [25–29], conjugated polymers containing 1,8-naphthalimide derivatives appear promising owing to the possibility of energy transfer from the conjugated backbone to the low-band-gap 1,8-naphthalimide moieties and the already observed high PL and EL efficiency in these polymers [30,31]. In order to study the light-emitting properties of 1,8-naphthalimide-containing conjugated polymers and to explore its use in potential PLED applications, we designed and synthesized in this study a 1,8-naphthalimide-containing carbazole monomer, i.e. 4-(3,6-dibromocarbazol-9-yl)-*N*-(4′-*tert*-butyl-phenyl)-1,8-naphthalimide (Br–CN), and co-polymerized it with 2,7-dibromo-9,9-dioctylfluorene (DBF) to afford a series of copolymers (CNPFs) containing different amount of 1,8-naphthalimide through the Yamamoto coupling reaction (Scheme 1). The feed ratio of Br–CN was kept low at 0.05, 0.1, 0.5 and 1 mol%, respectively, during the co-polymerization. Poly(9,9′-dioctylfluorene) (PF) was also prepared for comparison purpose. The chemical structures of Br–CN and polymers are demonstrated by ^1H NMR. However, due to the very low feed ratio of Br–CN in co-polymerizations, ^1H NMR did not give meaningful information about the exact contents of the segment of 4-(carbazol-9-yl)-*N*-(4′-*tert*-butyl-phenyl)-1,8-naphthalimide (CN) in the polymers. In IR spectra of CNPFs, the sign peaked at 1716 and 1678 cm^{-1} (the characteristic peaks of carbonyl in 1,8-naphthalimide unit) become clearer as the feed ratio of Br–CN increased, which verified the increasing contents of CN segment in the copolymer. Given the high molecular weights of these copolymers ($M_n = 25{,}000$–37,000 as determined by GPC, Table 1) and the high synthetic yields (>70%), we can assume that the final contents of CN in copolymers are the same as the feed ratios. All the polymers were readily soluble in common organic solvents (e.g. chloroform and tetrahydrofuran) and can form high-quality thin films by spin-coating.

The thermal properties of the resulting polymers were characterized by differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) in nitrogen (Table 1). The glass transition temperatures (T_gs) of copolymer CNPFs and BCNPF05 were found to be comparable to that (75 °C) of polyfluorene [8] and are in the range of 70–82 °C. All the polymers showed similar high onset temperature of decomposition (T_d) around 415 °C.

3.2. Photoluminescence properties

Due to the very low content (<1 mol%) of CN unit in the copolymers, CNPFs showed basically the same UV–vis spectrum as that of PF. Fig. 1 shows the absorption spectra of CNPF05, which contained 0.5 mol% of CN unit in the polymer, and PF in the films. Different from the UV–vis spectroscopy, photoluminescent (PL) spectra of CNPFs showed distinctively different pattern from that of PF (Fig. 2). All the CNPFs exhibited two PL peaks, with one at 437 nm attributable to the PL of PF and the other around



Scheme 1. Synthetic scheme for Br–CN and copolymer CNPFs. Reagents and conditions: (i) 4-*tert*-butyl-phenylamine, CH_3COOH, reflux; (ii) carbazole, K_2CO_3, 18-Crown-6, CuI, 180 °C for 12 h; (iii) Bu_4NBr_3, $CHCl_3$, 12 h; (iv) $Ni(COD)_2$, 1,5-cyclooctadiene, α,α'-dipyridyl, toluene, DMF, 80 °C for 4 days.

500 nm attributable to the PL of CN unit. From Fig. 2, it can be clearly seen that as the increase of CN contents in CNPFs the PL intensity decreased at 437 nm and increased at around 500 nm. At a CN content of 0.5 mol%, the PL peak in the low-energy band became dominant, with the PL intensity from CN unit being three times stronger than that from PF. Considering the very low CN content of 0.5 mol%, the energy transfer from PF backbone to CN appeared to be very efficient, which is further evidenced by the spectrum overlap between PF emission and the CN absorption (Fig. 3). A slight color change in the PL spectrum in the low energy band as the increase of CN content was observed from 500 nm for CNPF005 to 512 nm for CNPF1, which may be ascribed to the overlap between the two emission peaks and the change of the relative intensity of these two peaks.

3.3. Redox properties

Since, the redox potentials of a compound reflect the HOMO and LUMO energies and may be related to the electroluminescent (EL) properties, the electrochemical behavior of the resulting polymers and the small molecular CN were first studied by cyclic voltammetry (CV). Table 2 illustrates the typical redox properties and the calculated HOMO and LUMO energies of PF, CNPF05 and CN. All the copolymer CNPFs showed similar electrochemical behavior to that of PF rather than CN. For example, slight down-shifts of redox potentials were observed for CNPFs (e.g. 0.08 and 0.09 V for the oxidation and reduction potentials of CNPF05, respectively) in relative to those of PF, whereas a large difference (e.g. 1.2 V down-shift of the reduction potential for CNPF05) was revealed when compared to the redox properties of CN. Since, the difference between the onset reduction and oxidation potentials (E_g) reflects the emission frequency, it seems that the copolymer CNPFs and PF should exhibit similar EL properties due to their very similar E_gs.

3.4. EL properties and current–voltage to brightness (I–V–B) characteristics

For the study of EL properties of CNPFs, single-layer devices with the configuration of ITO/PEDOT/copolymer/-Ca/Al were fabricated. Quite different from what was expected from the redox studies, all EL devices based on CNPFs

Table 1
Molecular weights and thermal properties of polymers

Polymer	M_n[a]	M_w[a]	M_w/M_n[a]	T_d[b] (°C)	T_g[c] (°C)
CNPF005	31,412	130,695	4.16	418.65	76.88
CNPF01	30,402	119,415	3.93	420.33	70.60
CNPF05	25,273	104,722	4.14	415.52	75.45
CNPF1	37,018	169,517	4.58	412.02	77.80
BCNPF05	33,152	115,650	3.49	411.91	82.32

[a] Molecular weights and polydispersity indices determined by GPC in THF using polystyrene as the standard.
[b] Onset decomposition temperature measured by TGA under N_2.
[c] Glass transition temperature measured by DSC under N_2.

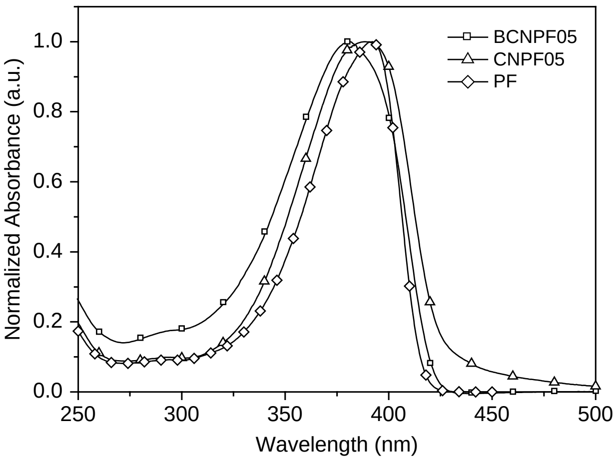


Fig. 1. UV–vis absorption spectra of CNPF05, BCNPF05 and PF in the film.

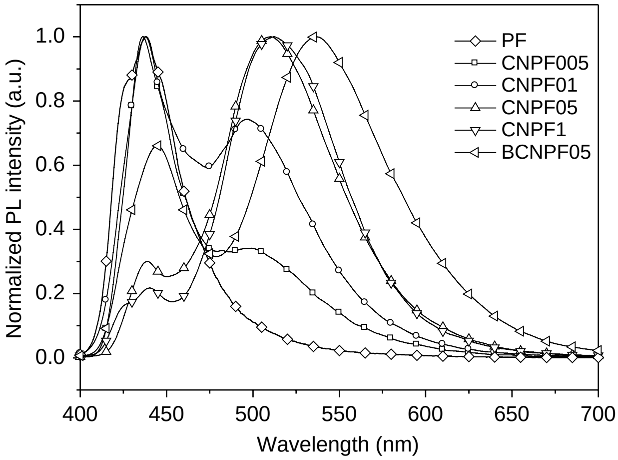


Fig. 2. Photoluminescence spectra of CNPFs, BCNPF05 and PF in the film.

exhibited a predominant light-emitting peak (around 510 nm) attributable to the CN unit (Fig. 4). In comparison with PL of CNPFs films, the emission pattern (i.e. the relative intensity of the two emission peaks attributable to PF and CN, respectively) of CNPFs in EL devices showed an even heavier dependence on the CN content. For example, at a CN content of 0.1 mol%, the EL intensity from CN is six times stronger than that from PF backbone; as the CN content was increased to 0.5 mol%, the EL from PF backbone was no more discernible and the device become purely green emitting attributable to the EL from CN

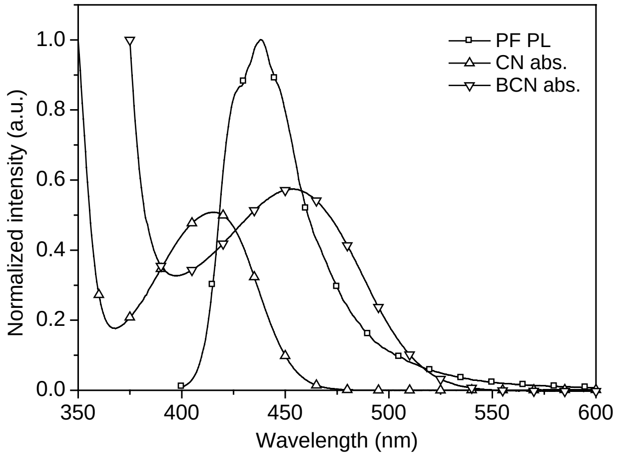


Fig. 3. Absorption of CN and BCN in toluene and PL spectra of PF.

Table 2
Electrochemical properties of PF, CNPF05, CN, BCNPF05 and BCN

Polymer	Eonset,ox (V)	HOMO (eV)	Eonset,red (V)	LUMO (eV)	E_g (eV)
PF	1.46	−5.80	−2.22	−2.12	3.68
CNPF05	1.37	−5.71	−2.30	−2.04	3.67
CN	1.41	−5.75	−1.13	−3.21	2.54
BCNPF05	1.42	−5.76	−2.25	−2.09	3.67
BCN	0.85	−5.19	−1.09	−3.25	1.94

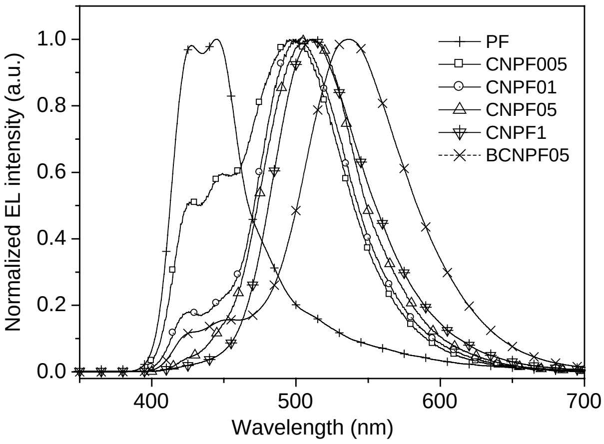


Fig. 4. Electroluminescence spectra of ITO/PEDOT/polymer/Ca/Al.

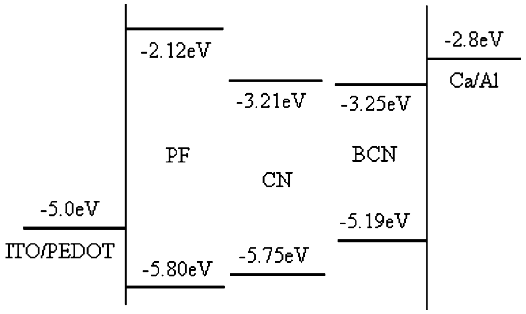


Fig. 5. Schematic diagram representing the potential metrically determined HOMO and LUMO energy of CN, BCN and PF relative to the work function of the electrodes used in the PLED fabricated from these materials. Potentials shown are relative to vacuum.

Table 3
Absorption, PL, and EL data of CNPFs and BCNPF05

Polymers	$PL_{max,film}$[a] (nm)	EL_{max} (nm)	CIE
CNPF005	436.5[b], 495.0	495.0	(0.18, 0.31) Bluish green
CNPF01	437.5[b], 497.0	501.0	(0.21, 0.42) Green
CNPF05	438.9, 510.5[b]	505.5	(0.21, 0.48) Green
CNPF1	439.5, 512.0[b]	512.4	(0.26, 0.50) Yellowish green
BCNPF05	444.0, 536.5[b]	536.0	(0.32, 0.51) Yellowish green

[a] $PL_{max,film}$ all exhibit two peaks: the short-wavelength contribute to PF backbone and the long-wavelength contributed to naphthalimide unit.

[b] The dominant peak in PL spectra.

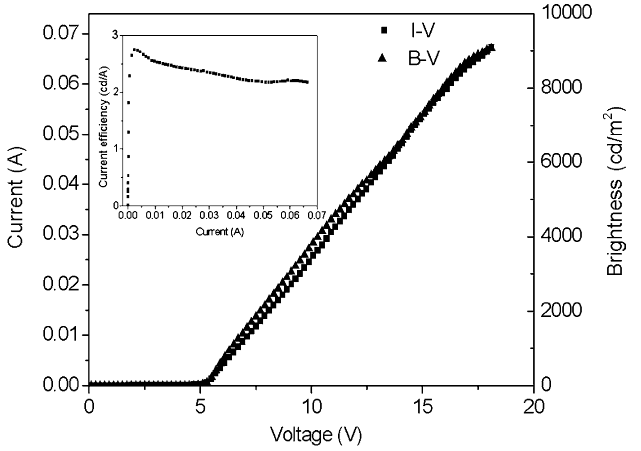
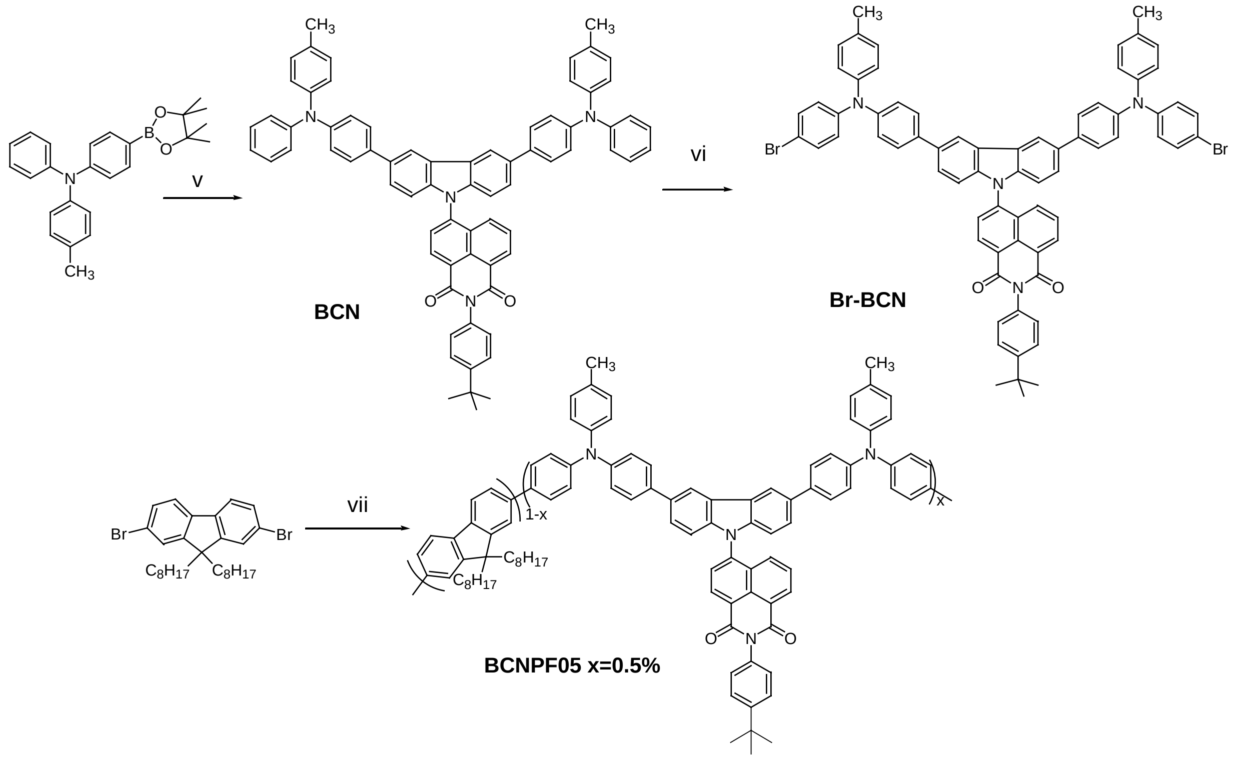


Fig. 6. Current–voltage–brightness characteristics of the device ITO/PEDOT/CNPF01/Ca: Al [inset is the EL efficiency-current property of the corresponding device].

Table 4
Device performance characteristics of the copolymer in ITO/PEDOT/polymer/Ca/Al device

Polymer	Turn-on voltage (V)	Maximum luminous efficiency (cd/A)	Maximum power efficiency (lm/W)	maximu luminance (cd/m^2)
CNPF005	3.5	2.51	1.41	7095
CNPF01	4.2	2.74	1.51	9104
CNPF05	4.4	2.17	0.90	8189
CNPF1	4.9	1.15	0.34	6648
BCNPF05	4.9	4.53	1.57	14,228

unit. This distinctively different light-emitting behavior of CNPFs in EL devices from their PL in films may be rationalized by the different light-emitting mechanism. For the PL of CNPFs in films, the green emission from CN is enabled by the Förster energy transfer process from the PF backbone to the low-band-gap CN unit, whereas for the EL of CNPFs in devices, charge trapping may occur due to the presence of low-band-gap CN in the copolymers, which led to the strong green emission, though the energy transfer can not be excluded. In the resulting OLED, electrons and holes are trapped in the CN unit with two manners: one is that the holes and electrons from respective electrodes are directly trapped by the 1,8-naphthalimide, leading to 1,8-naphthalimide emission; another is that the holes and electrons are firstly injected and transport along PF segments, and then trapped by the CN parts. And the later case is dominant, which can verified by the later improvement of device efficiency, when the CN contents are very low, emission from PF segments and CN parts can simultaneously observed. As the CN contents are increased to some extend, only CN emission can be observed. This charge trapping process in CNPF-based EL devices was verified by the analysis of the HOMO and LUMO energy level of small molecular CN and PF, which were obtained from the redox studies, in relative to the work function of the electrodes used in the EL device (Fig. 5). The HOMO and the LUMO of CN model fall within that of PF. The HOMO energy of CN is -5.75, 0.05 eV higher than that of PF, while the LUMO energy of CN is -3.21, 1.09 eV lower than that of PF, thus charges may be trapped by CN unit upon the application of a voltage and the electron–hole recombination at CN unit plays



Scheme 2. Synthetic scheme for Br–BCN and copolymer BCNPF05. Reagents and conditions: (v) Br–CN, Pd(PPh$_3$)$_4$, K$_2$CO$_3$, toluene, H$_2$O, 80 °C for 2 days, (vi) Bu$_4$NBr$_3$, CHCl$_3$, 12 h; (vii) Ni(COD)$_2$, 1, 5-cyclooctadiene, α,α'-dipyridyl, toluene, DMF, 80 °C for 4 days.

an important role in yielding the unique EL behavior. EL devices based on CNPF01 and CNPF05 emitted pure green color with a CIE coordinate of (0.21, 0.42) and (0.21, 0.48), respectively, while EL device based on CNPF1 emitted yellowish green color with a CIE of (0.26, 0.50) (Table 3). Thus, by a careful control of the CN content in the copolymers, pure green emitting EL materials can be obtained.

Fig. 6 shows the current–voltage–brightness characteristics of a single layer device of ITO/PEDOT/CNPF01/Ca/Al and Table 4 summarizes the device performances. The turn-on voltages increased with the increase of CN content and were in the range of 3.5–4.9 V. To some extend, both Förster energy transfer and charge trapping might take place at the same time, but the increase in the turn-on voltage with an increasing content of CN unit provides additional evidence for that charge trapping is the predominant process in this system. At a CN content of 0.1 mol%, the CNPF01-based EL device showed the best performances with a brightness of 9104 cd/m^2 at 18 V, the maximum luminous efficiency of 2.74 cd/A and a power efficiency of 1.51 lm/W.

In order to further improve the device performances, the electron and hole trapping at the low-band-gap unit should be balanced. From Fig. 5, the HOMO energy level of small molecular CN is only 0.05 eV higher than that of PF but the LUMO is 1.09 eV lower, which may lead to the trapping of more electrons than holes at the CN unit in the copolymers. And the resulting partly separation electrons and holes may decrease the recombination opportunity of charges and therefore limit the electroluminescence efficiency, which is very similar to the study of the device based on the copoly(aryl-ether)s consisting of alternate electron-transporting and hole-transporting fluorophores [34]. To overcome this problem, we designed and synthesized a new 1,8-naphthalimide-containing monomer, i.e. 4-{3,6-bis-[4″-(4‴-bromophenyl-*p*-tolyl-amino)-phenyl]-carbazol-9-yl}-*N*-(4′-*tert*-butyl-phenyl)-1,8-naphthalimide (Br–BCN) (Scheme 2). The introduction of triarylamine into the structure was believed to be able to improve the hole trapping efficiency in the resulting copolymer, which was evidenced by its energy levels calculated from the CV results (Fig. 5). Thus, a copolymer BCNPF05 was prepared by co-polymerization of DBF and 0.5 mol% of Br–BCN through the Yamamoto coupling reaction (Scheme 2). The characterizations and luminescent properties of BCNPF05 are given in Tables 1–4 and Figs. 1–4. It should be noted that, different from that of the CNPF containing the same amount of 1,8-naphthalimide (i.e. 0.5 mol.%), the EL of BCNPF05 still show the emitting peak attributable to the PF backbone. Fig. 7 shows the current–voltage–brightness characteristics of a device of ITO/PEDOT/BCNPF05/Ca/Al. As expected, due to a more balanced electron and hole trapping, the device based on BCNPF05 exhibited much better performances than devices based on CNPF05. The brightness was as high as 14228 cd/m^2 at 23 V, the maximum luminous efficiency was increased to 4.53 cd/A and the power efficiency is 1.57 lm/W.

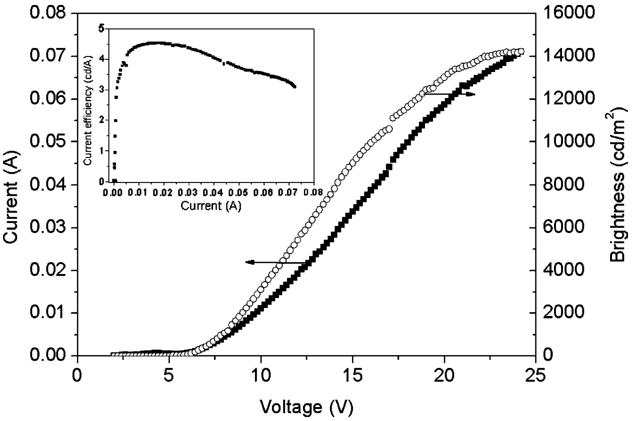


Fig. 7. Current–voltage–brightness characteristics of the device ITO/PEDOT/BCNPF05/Ca: Al [inset is the EL efficiency-current property of the corresponding device].

4. Summary

Two low-band-gap 1,8-naphthalimide-containing monomers, i.e. 4-(3,6-dibromocarbazol-9-yl)-*N*-(4′-*tert*-butyl-phenyl)-1,8-naphthalimide (Br–CN) and 4-{3,6-bis-[4″-(4‴-bromophenyl-*p*-tolyl-amino)-phenyl]-carbazol-9-yl}-*N*-(4′-*tert*-butyl-phenyl)-1,8-naphthalimide (Br–BCN), were designed, synthesized and co-polymerized with 2,7-dibromo-9,9-dioctylfluorene to yield a series of light-emitting conjugated polymers. It was found that the introduction of a small amount (e.g. <1%) of 1,8-naphthalimide group into the polyfluorene structure could effectively tune the emitting color from blue to green. For photoluminescence, the color tuning went through the Förster energy transfer mechanism, while for electroluminescence (EL), the color tuning was dominated by a charge trapping scheme. By a careful control of the feed ratio of Br–CN in the range of 0.1–0.5 mol%, the resulting copolymer-based EL device could emit pure green color light. In comparison with Br–CN-based copolymers, Br–BCN-based polymers had a more balanced electron and hole trapping process and therefore exhibited better EL device performances.

Acknowledgements

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