Articles

Syntheses and Characterization of Alkoxyphenyl-Substituted PCPP with Stabilized Blue Emission and Its Derivatives with Ketone Unit in the Main Chain

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ABSTRACT: The syntheses and characterization of alkoxyphenyl-substituted PCPP, poly(2,6-(4,4-bis(4-((2-ethylhexyl)oxy)phenyl)-4*H*-cyclopenta[*def*]phenanthrene)) (BEHP-PCPP), with stabilized blue emission and its derivatives with ketone unit in the main chain, poly(2,6-(4,4-bis(4-((2-ethylhexyl)oxy)phenyl)-4*H*-cyclopenta[*def*]phenanthrene)-*co*-2,6-(cyclopenta[*def*]phenanthren-4-one)) (K-PCPPs), are presented. The device utilizing BEHP−PCPP provided stabilized blue emission and incorporation of small amount of the ketone unit in the backbone generated variable emission colors. The purity of the monomer is very important for the stable blue emission, and it was possible to purify the bis(alkoxyphenyl)-substituted monomer by recrystallization to remove monoarylated impurity completely. The PL spectra of BEHP-PCPP thin film did not show any peak in the region of 500−600 nm even after annealing for 9 h at 150 °C in air. The OLED with the configuration of ITO/PEDOT:PSS/BEHP-PCPP/Ca/Al generates EL emission with maximum peak at 430 nm, turn-on voltage of 5.0 V, maximum brightness of 1035 cd/m^2 at 9.0 V, efficiency of 0.11 cd/A at 75 mA/cm^2, and CIE coordinates of ($x = 0.20$, $y = 0.16$), without any filtering, which are quite close to those of the standard blue ($x = 0.14$, $y = 0.08$). Moreover, the OLED with BEHP-PCPP displays stabilized blue emission without showing any peak in the region of 500−600 nm even after annealing the device for 23 h at 150 °C or operation of the device for 50 min with 8 V. The device of K1-PCPP (BEHP-PCPP with 1% of ketone unit) show EL emission with maximum peak at 540 nm, CIE coordinates of ($x = 0.36$, $y = 0.57$), turn-on voltage of 10.5 V, maximum brightness of 1143 cd/m^2, and luminescence efficiency of 0.11 cd/A. The device of K001-PCPP (BEHP-PCPP with 0.01% of ketone unit) shows EL emission with maximum peaks at 430 and 520 nm, CIE coordinates of ($x = 0.26$, $y = 0.38$) which are close to those of standard white, turn-on voltage of 5.5 V, maximum brightness of 1143 cd/m^2, and luminescence efficiency of 0.53 cd/A.

Introduction

There have been many efforts to utilize conjugated polymers as active materials of electronic devices including transistors[1] and organic light-emitting diodes (OLEDs).[2,3] OLEDs have many advantages due to their processability, low driving voltage, wide viewing angle, and easy color tunability over the full range.[4−9] Much research efforts have been directed toward the synthesis of stabilized blue light-emitting polymers because they are essential for the full color generation either as patterned RGB emitters or for the use as the host materials.[10−13]

Polyfluorenes (PFs)[14] are generally considered as the most attractive class of blue materials in organic light-emitting devices (OLEDs) due to high photoluminescence (PL) efficiency and good charge transport.[15,16] Nevertheless, PFs have a drawback to cause long wavelength emission around 550 nm either during annealing or operation of the device. This long wavelength emission results in the color change, from wanted blue to unwanted blue-green, and a drop of electroluminescence (EL) quantum efficiency of the device.[17−19] To overcome the problem of the low energy emission, caused by the formation of keto defect sites[20] or aggregates/excimers,[16a] various types of approaches have been utilized including the use of longer and branched side chains or bulky substituents,[21] the copolymerization techniques,[22] end-capping of PFs with bulky groups,[23] siprofluorenes,[24] and the control of the molecular weight distribution of PFs.[25] Especially, the attachment of alkoxyphenyl groups at the 9-position of the fluorene has been reported to show stable blue emission, after annealing the polymer films, which suggests that alkoxyphenyl groups effectively suppress long-wavelength emission.[26] Elimination of the impurities in the monomer, which is partially alkylated fluorene,[20] and complete dialkylation of the fluorene momomer have been reported to show the suppression of the emission attributed to the defects in PL and EL of PFs.[27]

Recently, we synthesized a new blue-emitting polymer, poly(2,6-(4,4-bis(2-ethylhexyl)-4*H*-cyclopenta[*def*]phenanthrene)) (PCPP),[28,29] with a rigid backbone, which generates

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stabilized and efficient blue electroluminescence without exhibiting any peak in the long-wavelength region even after prolonged annealing the device or operation of the devices in air. But one of the basic problems of PCPP, with dialkyl groups in the monomer, is that it is extremely difficult to have complete elimination of the monoalkylated form of the PCPP monomer, since the mono- and dialkylated monomers are liquids, and very nonpolar, and cannot be purified by recrystallization.

In this paper, new PCPP derivative, poly(2,6-(4,4-bis(4-((2-ethylhexyl)oxy)phenyl)-4*H*-cyclopenta[*def*]phenanthrene)) (BEHP-PCPP), with complete substitution at 4-position of CPP by using bis(alkoxyphenyl) groups, was prepared by Yamamoto coupling reaction. In the synthesis of BEHP-PCPP, bis(phenol) intermediate, with high polarity, was completely purified, from monophenol impurity, by recrystallization. After dialkylation of the clean bis(phenol) intermediate, pure bis(alkoxyphenyl)-substituted monomer was obtained by additional recrystallization, which is quite important for the generation of stabilized blue emission. In addition to this, poly(2,6-(4,4-bis(4-((2-ethylhexyl)oxy)-phenyl)-4*H*-cyclopenta[*def*]phenanthrene)-*co*-2,6-(cyclopenta[*def*]phenanthren-4-one))s, with ketone unit in the backbone, are reported. By incorporation of the ketone defect sites, emission property of BEHP-PCPP can be changed dramatically through energy transfer to generate white emission color.[30,31]

Experimental Section

Materials and Instruments. All used reagents, including 4*H*-cyclopenta[*def*]phenanthrene, were purchased from Aldrich and used without further purification. Solvents were purified by normal procedure and handled under moisture-free atmosphere. IR spectra were recorded on a Perkin-Elmer 16F PC FT-IR spectrometer with samples prepared as KBr pellet. ^{1}H and ^{13}C NMR spectra were recorded with a Varian Gemini-300 (300 MHz) spectrometer, and chemical shifts were recorded in ppm units with TMS as the internal standard. Flash column chromatography was performed with Merck silica gel 60 (particle size 230−400 mesh ASTM) with ethyl acetate/hexane gradients. Analytical thin layer chromatography (TLC) was conducted using Merck 0.25 mm silica gel 60F precoated aluminum plates with fluorescent indicator UV254. UV spectra were recorded with a Varian CARY-5E UV/vis spectrophotometer. The PL spectra of the devices were measured under a nitrogen atmosphere using the HITACHI F-7000 detection system. For PL spectrum measurements, a xenon lamp was used as the excitation source, and incident beam took the maximum absorption peak of the polymers. The EL spectra of the devices were measured under a nitrogen atmosphere using the PR655 SpectraScane detection system. For the EL experiment, poly(3,4-ethylenedioxythiophene) (PEDOT) doped with poly(styrenesulfonate) (PSS), as the hole-injection-transport layer, was introduced between emissive layer. ITO glass substrate was cleaned with the detergent, ultrasonicated in deionized water, acetone, and isopropyl alcohol, and dried in the vacuum oven. An isopropyl solution of the PEDOT/PSS was spin-coated on the surface-treated ITO substrate in air. On top of the PEDOT/PSS layer, the emissive polymer film was obtained by spin-casting chlorobenzene solution of the polymer under a nitrogen atmosphere in a glovebox. The emissive polymer thin film prepared had a uniform surface with a thickness of around 110 nm. The thickness of the devices was measured using the Surfcorder ET3000. The emissive film was dried in vacuum, and aluminum electrodes were deposited on the top of the polymer films through a mask by vacuum evaporation at pressures below 10^{-7} Torr, yielding active areas of 4 mm^2. For the determination of device characteristics, current−voltage ($I-V$) characteristics were measured using a Keithley 236 source measure unit. Cyclic voltammetric waves were produced by using a EG&G Parc model 273 potentiostat/galvanostat at a constant scan rate of 80 mV/s. The differential scanning calometry analysis was performed under a nitrogen atmosphere (50 mL/min) on a DSC 822 at heating rates of 10 °C/min. Thermogravimetric analysis was performed with a Dupont 951 TGA instrument in a nitrogen atmosphere at a heating rate of 10 °C/min to 700 °C. FAB mass spectra were determined using at Korea Basic Science Institute Seoul Branch and Korea Basic Science Institute Daegu Branch.

Synthesis of 8,9-Dihydro-4*H*-cyclopenta[*def*]phenanthrene (2).[28] A stirred solution of 1.0 g (5.3 mmol) of 4*H*-cyclopenta-[*def*]phenanthrene (**1**), 10% palladium charcoal (0.50 g), and methanol (20 mL) was shaken for 20 h at room temperature under a hydrogen atmosphere (4 atm). After removal of the catalyst by filtration, the methanol was evaporated under reduced pressure. The residue was purified by flash column chromatography (30 × 200 mm column, SiO$_2$, 100% of *n*-hexane) to give 0.90 g (87%) of compound **2**, colorless oil; mp 134 °C, R_f 0.44 (SiO$_2$, 100% of *n*-hexane). FT-IR (KBr pellet, cm^{-1}): 3043, 3017, 2925, 2888, 2830, 2830, 1452, 1432, 1389, 810, 767, 726, 693. ^{1}H NMR (300 MHz, CDCl$_3$), δ (ppm): 3.18 (s, 4H), 3.92 (s, 2H), 7.17 (d, 2H, $J = 7.4$ Hz), 7.24 (t, 2H, $J = 7.4$ Hz), 7.37 (d, 2H, $J = 7.4$ Hz). ^{13}C NMR (75 MHz, CDCl$_3$), δ (ppm): 26.51, 37.69, 122.95, 124.92, 127.51, 130.76, 139.65, 140.67. HRMS (*m*/*z*, EI$^+$) calcd for $C_{15}H_{12}$ 192.0939; found 192.0943.

Synthesis of 2,6-Dibromo-8,9-dihydro-4*H*-cyclopenta[*def*]phenanthrene (3).[28] To prepare copper bromide adsorbed on alumina,[32] a solution of 10 g of copper bromide in 30 mL of distilled water was treated with neutral alumina (20 g, Merck aluminum oxide 90 active neutral) at room temperature. The reaction mixture was concentrated at 80 °C under reduced pressure. The resulting residue was dried under vacuum (4 Torr) at 100 °C for 15 h to generate the copper bromide adsorbed on alumina. To a stirred solution of 0.90 g (4.6 mmol) of 8,9-dihydro-4*H*-cyclopenta[*def*]phenanthrene (**2**) in 80 mL of carbon tetrachloride at room temperature was added 11.67 g of copper bromide adsorbed on alumina. After 5 h at 80 °C, the solid was filtered and washed with 2 × 30 mL of carbon tetrachloride. The combined organic phase was concentrated under reduced pressure, and obtained residue was purified by flash column chromatography (30 × 200 mm column, SiO$_2$, 100% of *n*-hexane) to give 1.5 g (93%) of compound **3**, pale yellow solid; mp 184 °C, R_f 0.50 (SiO$_2$, 100% of *n*-hexane). FT-IR (KBr pellet, cm^{-1}): 2925, 2894, 2828, 1574, 1433, 1411, 1394, 1065, 861, 839, 788. ^{1}H NMR (300 MHz, CDCl$_3$), δ (ppm): 3.08 (s, 4H), 3.83 (s, 2H), 7.46 (s, 2H), 7.47 (s, 2H). ^{13}C NMR (75 MHz, CDCl$_3$), δ (ppm): 25.95, 37.35, 121.33, 126.43, 128.43, 131.91, 137.56, 141.81. HRMS (*m*/*z*, EI$^+$) calcd for $C_{15}H_{10}Br_2$ 347.9149; found 347.9153.

Synthesis of 2,6-Dibromo-4*H*-cyclopenta[*def*]phenanthrene (4). To a stirred solution of 1.5 g (4.3 mmol) of 2,6-dibromo-8,9-dihydro-4*H*-cyclopenta[*def*]phenanthrene (**3**) in 30 mL of carbon disulfide at room temperature was added dropwise 0.27 mL (5.2 mmol) of Br$_2$ for 2 h. After stirring for 1 h, the reaction mixture was concentrated under reduced pressure, and the residue was purified by flash column chromatography (30 × 150 mm column, SiO$_2$, 100% of *n*-hexane) to give 1.2 g (80%) of compound **4**, pale yellow solid; mp 210 °C, R_f 0.53 (SiO$_2$, 100% of *n*-hexane). FT-IR (KBr pellet, cm^{-1}): 3043, 2926, 1570, 1419, 1403, 1309, 1211, 1063, 863, 831, 808, 711, 688. ^{1}H NMR (300 MHz, CDCl$_3$), δ (ppm): 4.32 (s, 2H), 7.75 (s, 2H), 7.80 (s, 2H), 7.99 (s, 2H). ^{13}C NMR (75 MHz, CDCl$_3$), δ (ppm): 37.16, 125.31, 125.62, 126.41, 127.97, 128.97, 132.91, 143.03. HRMS (*m*/*z*, EI$^+$) calcd for $C_{15}H_8Br_2$ 345.8993; found 345.8993.

Synthesis of 2,6-Dibromo-cyclopenta[*def*]phenanthren-4-one (5). To a stirred solution of 1.2 g (3.5 mmol) of 2,6-dibromo-4*H*-cyclopenta[*def*]phenanthrene (**4**) in 100 mL of benzene was added 5.0 g (58 mmol) of activated manganese oxide (MnO$_2$). The reaction mixture was refluxed for 12 h and concentrated under reduced pressure. The residue was purified by flash column chromatography (30 × 150 mm column, SiO$_2$, 100% of methylene chloride) to give 1.0 g (80%) of compound **5**, red solid; mp 166 °C, R_f 0.2 (SiO$_2$, 100% of *n*-hexane). FT-IR (KBr pellet, cm^{-1}): 3442, 1720, 1628, 1454, 1417, 1218, 1066, 881, 773, 678. ^{1}H NMR (300 MHz, CDCl$_3$), δ (ppm): 7.72 (s, 2H), 7.90 (s, 2H), 8.10 (s, 2H). ^{13}C NMR (75 MHz, benzene-d_6), δ (ppm): 124.27, 126.72, 126.79, 129.52, 133.97, 125.14, 137.89, 190.08. HRMS (*m/z,* FAB$^+$) calcd for $C_{15}H_6Br_2O$ 359.8785; found 359.8781.

Synthesis of 2,6-Dibromo-4,4-bis(4-hydroxyphenyl)-4*H*-cyclopenta[*def*]phenanthrene) (6). To a stirred solution of 1.0 g (2.8 mmol) of 2,6-dibromo-cyclopenta[*def*]phenanthren-4-one (**5**) in 20 mL of phenol was added 0.76 g (5.6 mmol) of $ZnCl_2$. The reaction mixture was heated at 50 °C, and then dry hydrogen chloride was bubbled for about 3 h. After concentration using reduced pressure, the residue was purified by flash column chromatography (30 × 180 mm column, SiO_2, 33% ethyl acetate/*n*-hexane) and recrystallization with ether to give 1.2 g (84%) of compound **6**, white solid; R_f 0.2 (SiO_2, 33% ethyl acetate/*n*-hexane). FT-IR (KBr pellet, cm^{-1}): 3853, 3648, 3277, 3032, 1574, 1508, 1230, 1066, 899, 858, 762, 707. ^{1}H NMR (300 MHz, acetone-d_6), δ (ppm): 6.74 (d, 4H, $J = 8.7$ Hz), 7.09 (d, 4H, $J = 8.7$ Hz), 7.80 (d, 2H, $J = 1.2$ Hz), 8.00 (s, 2H), 8.15 (d, 2H, $J = 1.2$ Hz) 8.35 (s, 2H, OH). ^{13}C NMR (75 MHz, acetone-d_6), δ (ppm): 68.56, 116.22, 122.75, 126.69, 126.84, 127.16, 129.84, 130.11, 134.48, 135.54, 153.05, 157.49. HRMS (*m/z,* FAB$^+$) calcd for $C_{27}H_{16}Br_2O_2$ 529.9517; found 529.9518.

Synthesis of 2,6-Dibromo-4,4-bis(4-((2-ethylhexyl)oxy)phenyl)-4*H*-cyclopenta[*def*]phenanthrene (7). To a stirred solution of 1.2 g (2.3 mmol) of 2,6-dibromo-4,4-bis(4-hydroxyphenyl)-4*H*-cyclopenta[*def*]phenanthrene (**6**) in 100 mL of acetone were added 0.35 g (2.3 mmol) of NaI, 4.9 g (1.4 mmol) of Cs_2CO_3, and 1.7 mL (9.3 mmol) of 2-ethylhexyl bromide. The reaction mixture was refluxed for 24 h and concentrated under reduced pressure. The obtained residue was purified by flash column chromatography (30 × 180 mm column, SiO_2, 100% of *n*-hexane) to give 0.46 g (26%) of compound **7**, white solid; mp 143 °C, R_f 0.74 (SiO_2, 100% of *n*-hexane). FT-IR (KBr, cm^{-1}): 3750, 2960, 2930, 2850, 1610, 1580, 1510, 1470, 1410, 1300, 1280, 1170, 1030, 854, 764, 729. ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 0.85−0.91 (m, 12H), 1.25−1.51 (m, 16H), 1.65−1.69 (m, 2H), 3.78 (d, 4H, $J = 5.8$ Hz), 6.78 (d, 4H, $J = 8.8$ Hz), 7.12 (d, 4H, $J = 8.8$ Hz) 7.66 (s, 2H), 7.79 (s, 2H), 7.98 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm): 11.33, 14.30, 23.26, 24.13, 29.29, 30.72, 39.58, 67.76, 70.57, 114.64, 122.46, 125.95, 126.15, 126.51, 129.11, 129.27, 134.08, 135.71, 151.89, 158.78. HRMS (*m/z,* FAB$^+$) calcd for $C_{43}H_{48}Br_2O_2$ 754.2021; found 754.2000.

Synthesis of Poly(2,6-(4,4-bis(4-((2-ethylhexyl)oxy)phenyl)-4*H*-cyclopenta[*def*]phenanthrene)) (BEHP-PCPP). To a stirred solution of 240 mg (0.88 mmol) of bis(1,5-cyclooctadiene)nickel(0) ($Ni(COD)_2$) in 5 mL of dry DMF were added 140 mg (0.88 mmol) of 2,2′-dipyridyl and 0.11 mL (0.88 mmol) of 1,5-cyclooctadiene. The reaction mixture was heated to 80 °C for half an hour to form the purple complex.[33] To the reaction mixture was added 300 mg (0.40 mmol) of monomer **7** in 5 mL of toluene. After 3 days heating at 80 °C, 300 mg of 9-bromoanthracene, the end-capper, in 5 mL of anhydrous toluene was added to the reaction mixture. The reaction mixture was further heated at 80 °C for 24 h. After cooling to room temperature, the reaction mixture was poured into the solution of 100 mL of aqueous HCl solution (35%), 100 mL of acetone, and 200 mL of methanol and stirred for 3 h. The solid was filtered and dissolved with a minimum amount of chloroform. A minimum amount of methanol was added to generate precipitation. The white solid was purified by Soxhlet extraction with methanol and dried in vacuum for 48 h to generate 160 mg of BEHP-PCPP, white powder.

Synthesis of Poly(2,6-(4,4-bis(4-((2-ethylhexyl)oxy)phenyl)-4*H*-cyclopenta[*def*]phenanthrene)-*co*-2,6-(cyclopenta[*def*]phenanthren-4-one)) (K-PCPPs). To a stirred solution of 242 mg (0.88 mmol) of bis(1,5-cyclooctadiene)nickel(0) ($Ni(COD)_2$) in 5 mL of dry DMF were added 137 mg (0.88 mmol) of 2,2′-dipyridyl and 0.11 mL of (0.88 mmol) of 1,5-cyclooctadiene. The reaction mixture was heated at 80 °C for half an hour to form a purple complex. To the reaction mixture were added the monomers with different feed ratios of **5** and **7** (total amount of 0.40 mmol) in 5 mL of toluene. The reaction mixture was further heated at 80 °C for 3 days. After cooling to room temperature, the reaction mixture was poured into the solution of 100 mL of aqueous HCl solution (35%), 100 mL of acetone, and 200 mL of methanol and stirred for 3 h. The solid was filtered, and dissolved with minimum amount of chloroform. A minimum amount of methanol was added to generate precipitation. The white solid was purified by Soxhlet extraction with methanol and dried in vacuum for 48 h to generate 100−150 mg of polymers.

Results and Discussion

Synthesis and Characterization of Polymers. The general synthetic routes toward the monomer and polymers are outlined in Scheme 1. For the preparation of BEHP-PCPP, in the first step, 4*H*-cyclopenta[*def*]phenanthrene (**1**)[34] was hydrogenated using 10% palladium on carbon to afford 8,9-dihydro-4*H*-cyclopenta[*def*]phenanthrene (**2**), which was brominated in carbon tetrachloride by alumina-supported copper(II) bromide to generate 2,6-dibromo-8,9-dihydro-4*H*-cyclopenta[*def*]phenanthrene (**3**) with excellent selectivity. Compound **3** was dehydrogenated with bromine in carbon disulfide to give 2,6-dibromo-4*H*-cyclopenta[*def*]phenanthrene (**4**), which was oxidized by activated MnO_2 to obtain 2,6-dibromocyclopenta[*def*]phenanthren-4-one (**5**). Compound **5** was treated with phenol in the presence of dry HCl and $ZnCl_2$ to generate 2,6-dibromo-4,4-bis(4-hydroxyphenyl)-4*H*-cyclopenta[*def*]phenanthrene (**6**), which was *o*-alkylated in acetone using 2-ethylhexyl bromide, Cs_2CO_3 and NaI to afford 2,6-dibromo-4,4-bis(4-((2-ethylhexyl)oxy)phenyl)-4*H*-cyclopenta[*def*]phenanthrene (**7**). The polymerization of the monomer **7** was affected under Yamamoto conditions,[35] using bis(1,5-cyclooctadiene)nickel(0) ($Ni(COD)_2$) catalyst, 2,2′-dipyridyl, and 1,5-cyclooctadiene. The end-capper, 9-bromoanthracene, was also used[36] to get the desired BEHP-PCPP.

K-PCPPs (K1-PCPP and K001-PCPP) with different compositions of monomer **5** and **7** contents were synthesized under Yamamoto coupling conditions, using bis(1,5-cyclooctadiene)nickel(0) ($Ni(COD)_2$), 2,2′-dipyridyl, and 1,5-cyclooctadiene. The molar feed ratios of monomer **5** to monomer **7** were 1:99, and 0.01:99.99, and the corresponding copolymers were referred to as K1-PCPP and K001-PCPP, respectively.

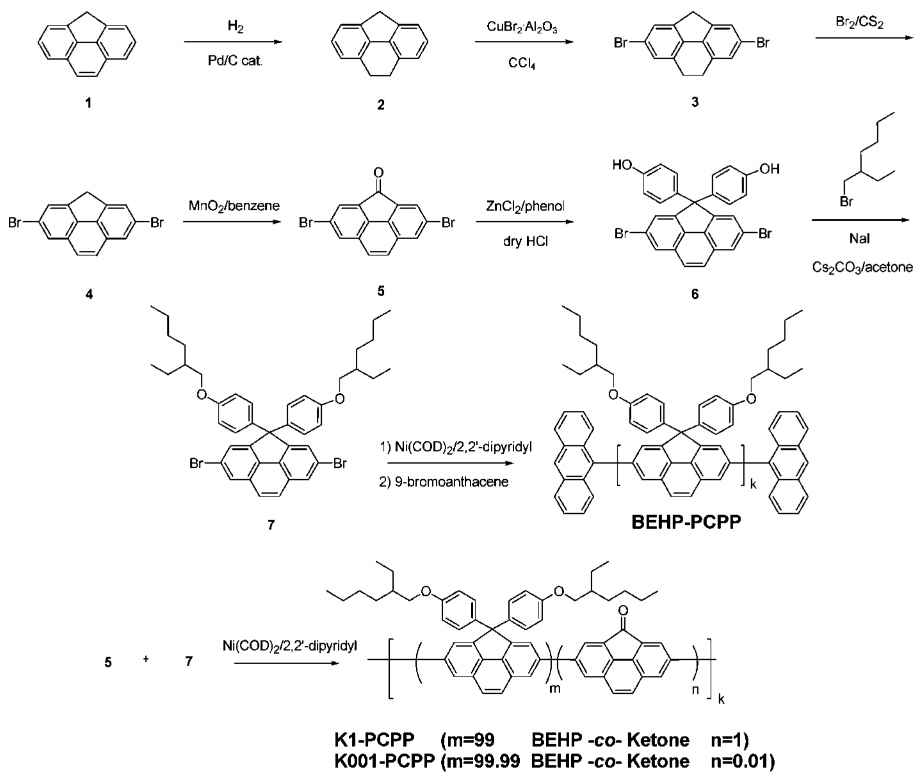
The ^{1}H NMR spectra of (a) the monomer and (b) the polymer were consistent with their chemical structures (Figure 1). The aromatic protons of PCPP backbone were labeled as “a”, “b”, and “c”. The protons of alkoxyphenyl moiety were labeled as “d”, “e”, and CH_2-O-Ar protons as “f”. And the aliphatic protons of the ethylhexyl groups were labeled as “g”, “h”, and “i”, respectively.

Molecular weight and polydispersity of the polymer were determined by gel permeation chromatography (GPC) analysis with a polystyrene standard calibration. As shown in Table 1, the number-average molecular weight (M_n) and the weight-average molecular weight (M_w) of the polymers were in the range of 42 000−72 000 (M_n) and 140 000−400 000 (M_w), respectively, with polydispersity indices (M_w/M_n) of 2.2−5.1. All the polymers were soluble in organic solvents such as chloroform, tetrahydrofuran, dichloromethane, and chlorobenzene.

The thermal properties of the polymers were evaluated by differential scanning calometry (DSC) and thermogravimetric analysis (TGA) in nitrogen. The decomposition temperatures (T_d), which correspond to a 5% weight loss upon heating during TGA, were in the range of 412−423 °C, and the glass transition temperatures (T_g) of the polymers were in the range of 70−72 °C (Table 1). The thermal data obtained for all polymers show that introduction of alkoxyphenyl groups on the rigid CPP backbone results in materials with high T_d values, which is essential for optimal behavior in OLEDs.

Optical and Photophysical Properties. The UV−vis absorption spectra of the polymers in THF solution and in thin film are presented in Figure 2. The absorption spectrum of

Scheme 1. Synthetic Routes for the Monomers and the Polymers



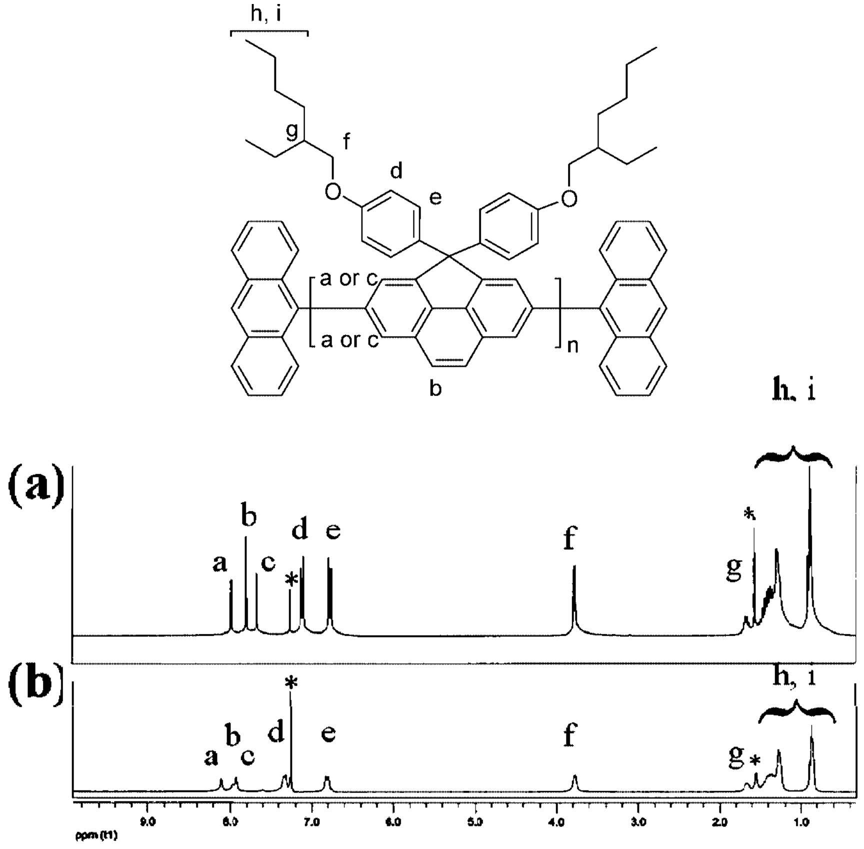


Figure 1. ^{1}H NMR spectra of (a) the monomer and (b) the polymer in $CDCl_3$. The solvent peak are denoted by an asterisk.

BEHP-PCPP in THF solution is similar to that of the film. BEHP-PCPP exhibits the maximum absorption peak at 366 nm, which is attributed to $\pi-\pi^*$ transition of the conjugated main chains, and additional absorption peaks at 296 and 311 nm due to $\pi-\pi^*$ transition of cyclopenta[*def*]phenanthrene (CPP) units.

In case of K-PCPPs, the absorption spectra of the copolymers are similar to that of BEHP-PCPP, indicating that small amount of ketone units in the backbone does not give much effect on the absorption spectra. The absorption onset wavelength of BEHP-PCPP was 406 nm, which corresponds to the band gap

Table 1. Characterization of the Polymers

copolymers	M_w[a]	M_n[a]	M_w/M_n[a]	T_g[b] (°C)	T_d[c] (°C)
BEHP-PCPP	140 000	66 000	2.2	72	423
K1-PCPP	400 000	72 000	5.1	71	412
K001-PCPP	220 000	42 000	5.1	70	400

[a] Molecular weights determined by GPC in THF using a calibration curve of polystyrene as the standard. [b] Glass transition temperature determined by DSC. [c] Decomposition temperature corresponding to 5% weight loss in N_2 determined by TGA.

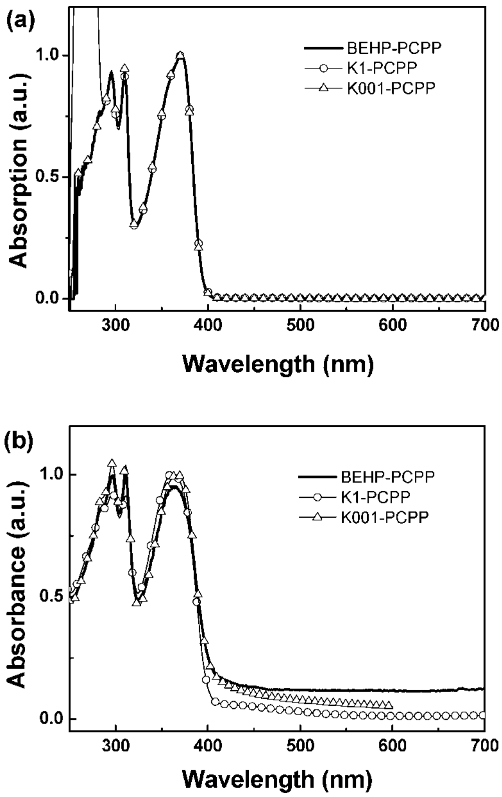


Figure 2. Normalized UV−vis absorption spectra of the polymers (a) in THF solution and (b) in thin solid state.

of 3.05 eV. The absorption onset wavelengths of the copolymers are 403 nm (K1-PCPP) and 406 nm (K001-PCPP), which correspond to the band gaps of 3.08 and 3.05 eV, respectively.

The PL spectra of the polymers in THF solutions and in thin films are shown in Figure 3. The PL spectrum of BEHP-PCPP in THF solution exhibited maximum peak at 400 nm and in thin film at 424 nm. Compared to the emission spectrum of the dilute solution, the thin film spectrum was red-shifted by 24 nm and broader than that of solution due to the inhomogeneous broadening effects in the solid state. In case of the copolymers with ketone unit, the PL emission spectra of K-PCPPs in THF solution show maximum peaks at around 400 nm. K1-PCPP in THF solution shows additional weak peak at 500−600 nm originating from the typical keto-defect structure. The PL spectrum of K1-PCPP in solid film shows a maximum peak at around 525 nm and an additional PL peak at 430−450 nm, which corresponds to BEHP-PCPP moiety. The PL spectrum of K1-PCPP shows decreased emission band at 430−450 nm caused by the energy transfer from the PCPP segments to the ketone segments. The significant increase in the relative intensity of the peak at 500−600 nm in solid films as compared to that of the solution may be ascribed to the strong self-absorption effect. The PL spectrum of K001-PCPP in solid film exhibits a maximum peak at 456 nm. The maximum peak of PL spectrum of K001-PCPP solid film is red-shifted by 56 nm as compared to that of THF solution. K001-PCPP did not show any noticeable peak at 500−600 nm, which is due to the lower ketone content of the copolymer than that of K1-PCPP. Generally, the low-energy emission from defects was enhanced in the film compared to corresponding solution because of the increased the probability of exited energy transfer to defects.

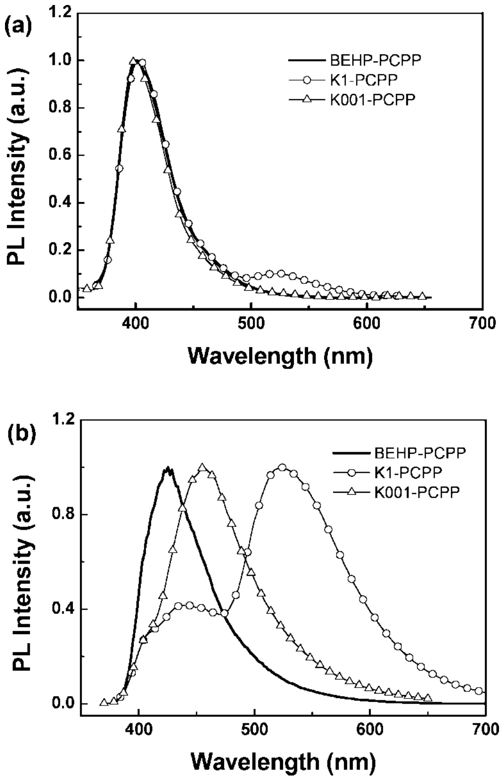


Figure 3. Normalized photoluminescence spectra of the copolymers (a) in THF solution and (b) in thin solid state.

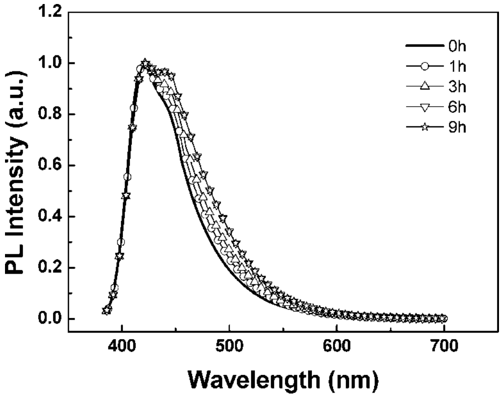


Figure 4. PL spectra of BEHP-PCPP after annealing the thin film at 150 °C in air.

The PL spectra of BEHP-PCPP film were also obtained after annealing the film for up to 9 h at 150 °C in air. As shown in Figure 4, the PL spectra of BEHP-PCPP did not show any peak around 550 nm, which corresponds to keto defect or aggregates/excimers even after annealing the film for 9 h at 150 °C in air. This stability is coming from the complete diarylation, which was achieved by the recrystallization of the monomer, and the bulkiness of the alkoxyphenyl groups which prevent the aggregation/keto-defect formation of the polymers.

Electrochemical Properties. The LUMO energy levels of the polymers were determined from the band gaps which were estimated from the absorption edges and the HOMO energy levels which were estimated from the cyclic voltammetry.[37] The

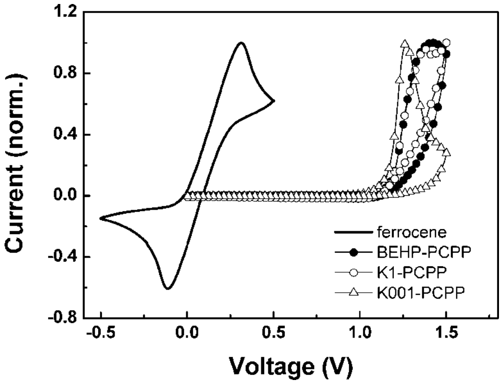


Figure 5. Cyclic voltammograms of the polymers recorded from thin films coated onto platinum wire electrodes in an electrolyte solution of Bu_4NBF_4 (0.10 M) in acetonitrile with a reference electrode of Ag/$AgNO_3$ (0.10 M) at room temperature. Scan rate = 80 mV/s.

Table 2. Electrochemical Potentials and Energy Levels of the Polymers

polymers	E_{onset}[a] (V)	HOMO[b] (eV)	LUMO[c] (eV)	E_g[d] (eV)
BEHP-PCPP	1.15	−5.91	−2.86	3.05
K1-PCPP	1.32	−6.08	−3.00	3.08
K001-PCPP	1.18	−5.94	−2.89	3.05

[a] Onset oxidation potentials measured by cyclic voltammetry. [b] Calculated from the oxidation potentials. [c] Calculated from the HOMO energy levels and E_g. [d] Energy band gaps were estimated from the onset wavelengths of the optical absorption.

CVs were performed with a solution of tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) (0.10 M) in acetonitrile at a scan rate of 80 mV/s at room temperature. Polymer films were prepared by dipping platinum working electrodes into the polymer solution, which was dissolved with minimum amount of THF soution and then air-drying. A platinum wire and an Ag/$AgNO_3$ electrode were used as the counter electrode and reference electrode, respectively. The energy level of the Ag/$AgNO_3$ reference electrode (calibrated by the FC/FC^+ redox system) was 4.76 eV below the vacuum level. The oxidation potentials derived from the onset of electrochemical p-doping are shown in Figure 5 and summarized in Table 2. HOMO levels were calculated according to the empirical formula $E_{HOMO}= -([E_{onset}]^{ox} + 4.76)$ (eV).[37,38] During the anodic scan, the oxidation onset potential of BEHP-PCPP was 1.15 V and exhibited irreversible p-doping process. HOMO energy level of the polymer was −5.91, eV. The absorption onset wavelength is 406 nm, which corresponds to band gap of 3.05 eV. The LUMO energy level, calculated from the value of the band gap and HOMO energy level, was −2.86 eV. The oxidation onset potentials of K1-PCPP and K001-PCPP were 1.32 V and 1.18 eV and exhibited irreversible p-doping process. HOMO energy levels of the copolymers were −6.08 and −5.94 eV. The absorption onset wavelengths are 403 and 406 nm, which correspond to band gaps of 3.08 and 3.05 eV. The LUMO energy levels, calculated from the values of the band gaps and HOMO energy levels, were −3.00 and −2.89 eV. The HOMO levels of K-PCPPs were lower than that of BEHP-PCPP, caused by the electron attractive effect of ketone unit in the backbone.

Electroluminescent Properties. The electroluminescence (EL) performance of the polymers was examined in the device configuration of ITO/PEDOT:PSS/polymers/Ca/Al. As shown in Figure 6, the EL spectrum of BEHP-PCPP exhibits maximum peak at 430 nm. The 1931 Commission Internationale de L'Eclairage (CIE) coordinates of the EL spectrum of BEHP-PCPP were ($x = 0.20$, $y = 0.16$) without any filtering, which are quite close to those of standard blue ($x = 0.14$, $y = 0.08$). In case of K1-PCPP, the EL spectrum did not show the emission peak at around 430 nm, which corresponds to PCPP segments and was completely transferred to the low-energy emission at around 550 nm. The EL spectrum of K001-PCPP exhibits maximum peak at 540 nm and additional peak at 430 nm, which correspond to the green and blue emission, respectively. The CIE coordinates of the EL spectra of K1-PCPP and K001-PCPP are ($x = 0.36$, $y = 0.57$) and ($x = 0.26$, $y = 0.38$), which correspond to the yellowish-green and bluish-white emission, respectively. K1-PCPP with high contents of the ketone unit exhibits dominant yellow emission. K001-PCPP generates reasonably well-balanced blue and green emissions which lead to bluish-white emission.

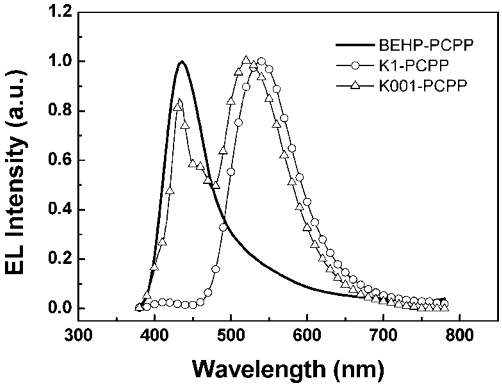


Figure 6. EL spetra of BEHP-PCPP, K1-PCPP, and K001-PCPP of OLEDs with the configuration of ITO/PEDOT:PSS/polymer/Ca/Al were used the voltages of the maximum brightness, 9.0, 14, and 8.5 V, respectively.

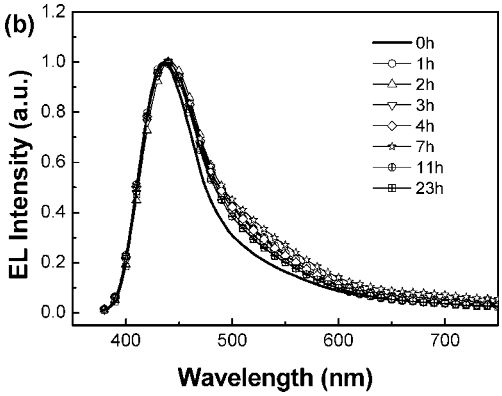


Figure 7. EL spectra of BEHP-PCPP after annealing the device at 150 °C in air.

The EL spectra of OLEDs were also obtained after annealing the device. As shown in Figure 7, the EL spectra of the device were not generating any obvious peak around 550 nm after annealing for 23 h at 150 °C in air. EL spectra on operation of the device are shown in Figure 8. After operation of the device for up to 50 min, the EL spectra of the device did not show any peak around 550 nm, which corresponds to keto defect or aggregates/excimers. In addition to this, the device with the polymer also displays stabilized blue EL emission even after operation with different voltages. These results indicate that the clean diarylation, which was achieved by the recrystallization of the monomer, and the bulkiness of the alkoxyphenyl groups prevent keto defect or aggregation effectively. In the synthesis of BEHP-PCPP, bis(phenol) intermediate, with high polarity, was completely purified from monophenol impurity by recrystallization. After dialkylation of the clean bis(phenol) intermediate, pure bis(alkoxyphenyl)-substituted monomer was obtained by additional recrystallization, which is quite important for the generation of stabilized blue emission. BEHP-PCPP with

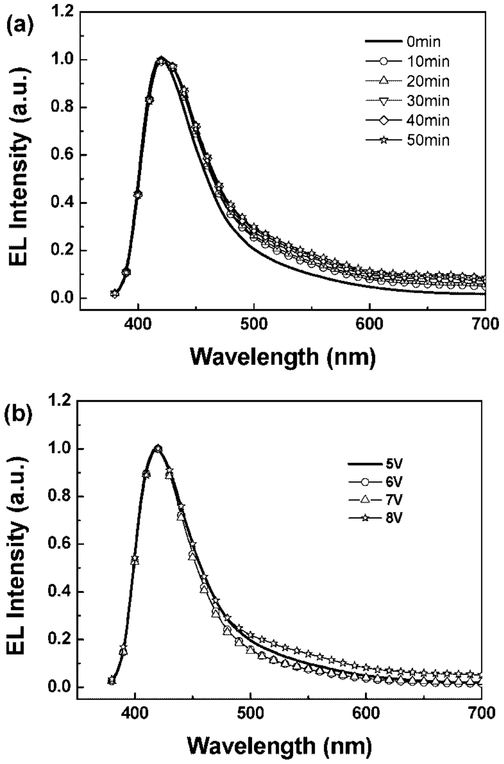


Figure 8. (a) EL spectra of the polymer after operation of the device for different time in air. (b) EL spectra of the polymer after operation of the device with different voltages.

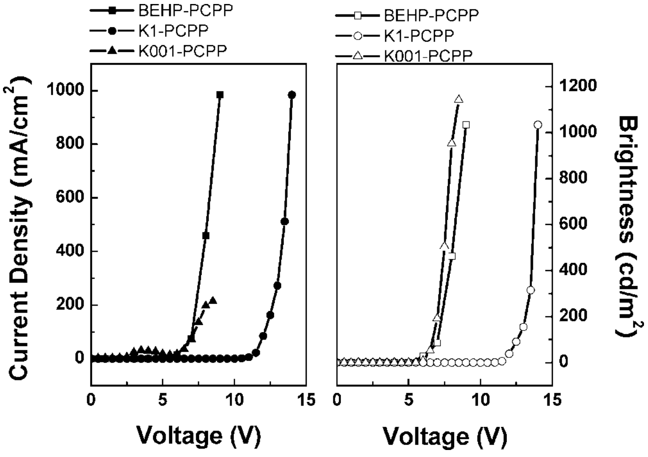


Figure 9. Current density−voltage−luminescence ($J-V-L$) characteristics.

stabilized blue emission could be effectively used in OLEDs application.

Current—Voltage—Luminance. The current density—voltage (J—V) and luminescence—voltage (L—V) characteristics of the devices with the configuration of ITO/PEDOT:PSS/polymers/Ca/Al are shown in Figure 9. BEHP-PCPP, K1-PCPP, and K001-PCPP showed the maximum brightness of 1035 cd/m^2 (at 9.0 V), 1035 cd/m^2 (at 14 V), and 1143 cd/m^2 (at 8.5 V) and turn-on voltage of 5.0, 10.5, and 5.5 V, respectively. As shown in Figure 10, the maximum luminescence efficiencies were 0.11 cd/A (BEHP-PCPP), 0.11 cd/A (K1-PCPP), and 0.53 cd/A (K001-PCPP). In case of K001-PCPP, the considerable increase in efficiency over those of K1-PCPP and BEHP-PCPP is due to the efficient energy transfer from the PCPP segments to the ketone units. The incorporation of ketone unit into BEHP-PCPP backbone is an effective approach to develop OLEDs with high EL efficiencies and variable emission colors.

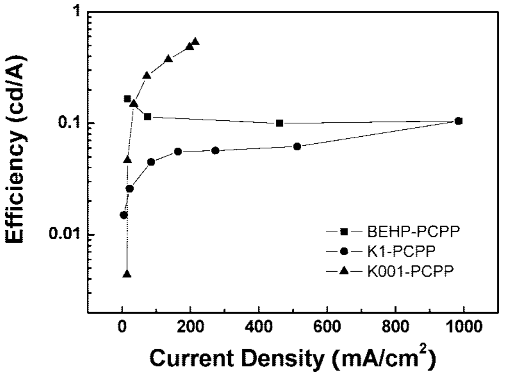


Figure 10. Efficiencies of OLEDs with the configuration of ITO/PEDOT:PSS/polymers/Ca/Al.

Conclusion

In conclusion, the syntheses and characterization of the conjugated polymer with stabilized blue emission and its derivatives with ketone unit in the main chain are presented. The OLED with the configuration of ITO/PEDOT:PSS/BEHP-PCPP/Ca/Al generates EL emission with maximum peak at 430 nm, turn-on voltage of 5.0 V, high maximum brightness of 1034 cd/m^2 at 9.0 V, efficiency of 0.11 cd/A at 75 mA/cm^2, and CIE coordinates of ($x = 0.20$, $y = 0.16$), without any filtering, which are quite close to those of the standard blue ($x = 0.14$, $y = 0.08$). Moreover, the OLED with BEHP-PCPP displays stabilized blue emission without any peak in the region of 500−600 nm even after annealing for 23 h at 150 °C or operation of the device for 50 min with 8 V. The purity of the monomer is very important for the stable blue emission, and it was possible to obtain the monomer with exceptionally high purity. The device of K1-PCPP (BEHP-PCPP with 1% of ketone unit) shows EL emission with maximum peak at 540 nm, CIE coordinates of ($x = 0.36$, $y = 0.57$), turn-on voltage of 10.5 V, maximum brightness of 1143 cd/m^2, and luminescence efficiency of 0.11 cd/A. The device of K001-PCPP (BEHP-PCPP with 0.01% of ketone unit) shows EL emission with peaks at 430 and 520 nm, CIE coordinates of ($x = 0.26$, $y = 0.38$) which are close to those of standard white, turn-on voltage of 5.5 V, maximum brightness of 1143 cd/m^2, and luminescence efficiency of 0.53 cd/A. The results indicate that the device utilizing BEHP-PCPP provided stabilized blue emission and incorporation of small amount of the ketone unit in the BEHP-PCPP backbone is an efficient strategy for the generation of variable emission colors.

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