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Synthesis of charge transporting block copolymers containing 2,7-dimethoxycarbazole units for light emitting device

ABSTRACT

into the emitting layer.

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1. Introduction

Numerous efforts on investigation for light emitting materials have been done for decades, thus the market for organic light emitting diode (OLED) applications has been getting larger and larger [1]. Polymeric light emitting materials have been attracted much attention because of good suitability for easy processing such as spin-coating and ink-jetting techniques. Nowadays, phosphorescent system dispersing a dopant such as Ir complex in polymer matrix prevails over other polymeric devices in external quantum efficiency (EQE) [2–6], but still remains behind compared with multi-layer organic small molecular devices fabricated by chemical vapor deposition. Single-layer polymer OLED device created by wet process can be an excellent candidate for mass production of devices, if the EQE is improved.

Copolymer or polymer blend systems consisting of several functional units such as hole and electron transporting components have been studied by many researchers [7–10]. In recent works, it was demonstrated that the device performance based on bipolar charge transporting block copolymers was significantly influenced by phase-separated morphology in the polymer layer, and that the nanophase separation of block copolymers facilitated charges recombination due to lowering charge transport in the emitting

layer, resulting in high EQE compared to the random copolymer systems without such a structure [11–13].

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The block copolymers consisting of 2,7-dimethoxycarbazole- and oxadiazole-containing segments as

hole and electron transporting units, respectively, were synthesized by NMRP manner. OLED devices

were fabricated using block copolymer, random copolymer, and polymer blend for matrix of the emitting

layer with $Ir(ppy)_3$ as a phosphorescent dopant in order to investigate morphological effect on the

performance. From the finding that the block copolymer system overwhelmed the others in EOE, we

assumed that a morphology with dimethoxycarbazole units assembled to the surface of PEDOT:PSS played a considerable role for effective recombination of charges as well as sufficient charge injection

In our previous work, block copolymers comprising triphenylamine and fluorinated oxadiazole units as hole and electron transport segments, respectively, were prepared to construct pseudo-layered structure by assembling oxadiazole segment into the air surface, which we assumed that achieve sufficient charge recombination as seen in multi-layered organic devices [14]. However, introduction of trifluoromethyl groups made the highest occupied molecular orbital (HOMO) level lower, which hamper effective charges recombination in the emitting layer because of poor hole confinement in spite of hole blocking layer. Here, we describe the synthesis and device evaluation of novel block copolymers including 2.7-dimethoxycarbazole units as hole transport component. Methoxy groups are expected to assist the self-assembly of hole transporting segment near poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) layer by hydrogen bonding with sulfonate groups [15,16].

2. Experimental section

2.1. Materials

Xylene and o-dichlorobenzene were distilled over calcium hydride and stored under nitrogen. Tetrahydrofuran (THF) and diethyl ether were used as distilled over sodium and





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benzophenone. As an initiator, N-(1-phenylethoxy)-N-(2-methyl-1-phenylpropyl)-t-butylamine (**10**) was prepared according to literature [17]. The other reagents were used as received.

2.2. Synthesis of 4-bromo-3-nitroanisole (1)

4-Methoxy-2-nitroaniline (168 g, 1.00 mol) was dissolved in 48% HBr aq. (300 mL), and cooled down to 0 °C. To this was added the solution of sodium nitrite (80.0 g, 1.16 mol) in water (100 mL) dropwise, and the solution was stirred at room temperature for 2 h. The resulting dispersion was poured in the solution of cupper (I) bromide (80.0 g, 0.558 mol) in 48% HBr aq. (80 mL) under nitrogen atmosphere, and stirred at 80 °C for 5 min. After cooling down to room temperature, the mixture was extracted with dichloromethane, and the organic layer was washed with sodium bicarbonate aq. and saturated brine. The organic layer was dried with magnesium sulfate and concentrated by rotary evaporator. The crude product was purified by vacuum distillation (150–151 °C/7.5 mmHg) affording a yellow solid. The yield was 167 g (72.1%). ¹H NMR (CDCl₃): δ 7.59 (d, 1H), 7.37 (d, 1H), 6.99 (dd, 1H), 3.86 (s, 3H).

2.3. Synthesis of 2-nitro-4,4'-dimethoxybiphenyl (2)

To the mixture of **1** (46.0 g, 0.198 mol) and 4-iodoanisole (60.0 g, 0.256 mol) was added cupper powder (30.0 g, 0.472 mol) at 180 °C, and stirred for 2 h. After heating up to 210 °C, another cupper powder (15.0 g, 0.236 mol) was added to the reaction mixture and stirring was continued for 2 h. The resulting mixture was cooling down to room temperature. After *N*-methylpyrrolidone (10.0 mL) was added, the mixture was extracted with acetone using Soxhlet extractor for 18 h. The solution was concentrated by rotary evaporator, and cooled down to 0 °C to recrystallize. The yellow crystal was collected and dried under vacuum. The yield was 28.0 g (54.5%). ¹H NMR (CDCl₃): δ 7.30 (d, 2H), 7.19 (d, 2H), 7.10 (d, 1H), 6.91 (d, 2H), 3.88 (s, 3H), 3.83 (s, 3H).

2.4. Synthesis of 2,7-dimethoxycarbazole (3)

To a two-necked flask equipped with a stopcock and a condenser were added **2** (46.5 g, 0.179 mol) and triethyl phosphite (135 mL, 0.788 mol) under nitrogen atmosphere, and the mixture was refluxed at 170 °C for 4 h. After cooling down to 0 °C, the resulting precipitation was collected by filtration. The white crystal was washed with methanol and dried at 100 °C under vacuum. The yield was 28.5 g (70.1%). ¹H NMR (DMSO-*d*₆): δ 10.98 (s, 1H), 7.83 (d, 2H), 6.93 (s, 2H), 6.72 (d, 2H), 3.80 (s, 6H).

2.5. Synthesis of 2,7-dimethoxy-N-(4-formylphenyl)carbazole (4)

To a two-necked flask equipped with a stopcock and a condenser were added **3** (27.3 g, 120 mmol), 4-bromobenzaldehyde (24.1 g, 130 mmol), palladium (II) acetate (0.270 g, 1.20 mmol), potassium carbonate (49.8 g, 120 mmol), and dry xylene (150 mL) under nitrogen atmosphere. Tri-*t*-butylphosphine (36.0 mL, 3.60 mmol, 0.1 M solution in xylene) was added, and the solution was stirred at 120 °C under reflux for 6 h. After cooling down to room temperature, the resulting mixture was extracted with chloroform and water. The organic layer was dried with magnesium sulfate and concentrated. The crude product was purified by silica gel column chromatography eluted with toluene to afford a yellow crystal. The yield was 16.7 g (42.0%). ¹H NMR (CDCl₃): δ 10.13 (s, 1H), 8.15 (d, 2H), 7.90 (d, 2H), 7.78 (d, 2H), 6.91 (m, 4H), 3.85 (s, 6H).

2.6. Synthesis of 2,7-dimethoxy-N-(4-vinylphenyl)carbazole (5)

To a three-necked flask equipped with a stopcock and a condenser were added methyltriphenylphosphonium bromide (25.9 g, 72.4 mmol), dry diethyl ether (48 mL), and dry THF (32 mL) under nitrogen atmosphere. Lithium diisopropylamide (32 mL, 24.1 mmol, 2.0 M solution in heptane, THF, ethylbenzene) was added at -25 °C, and stirred for 1 h. The solution of **4** (8.00 g, 24.1 mmol) in dry THF (80 mL) was added and the mixture was



Scheme 1. Synthesis of monomers 5 and 9.



Scheme 2. Preparation of block copolymer via NMRP.

stirred at room temperature for 36 h. The resulting mixture was extracted with chloroform and water, and the organic layer was dried with magnesium sulfate and concentrated by rotary evaporator. The crude product was purified by silica gel column chromatography twice eluted with chloroform, after that with toluene. Recrystallization from methanol afforded white crystal. The yield was 5.51 g (69.2%). ¹H NMR (CDCl₃): δ 7.89 (d, 2H), 7.65 (d, 2H), 7.51 (d, 2H), 6.89–6.79 (m, 5H), 5.87 (d, 1H), 5.37 (d, 1H), 3.82 (s, 6H).

2.7. Synthesis of 4-bromobenzoic hydrazide (6)

To a three-necked flask equipped with a stopcock and a condenser were added ethyl 4-bromobenzoate (25.0 g, 109 mmol), hydrazine monohydrate (40.0 mL, 825 mmol), and methanol (220 mL) under nitrogen atmosphere, and the mixture was stirred at 40 °C for 16 h. After methanol was concentrated, the precipitation was collected by vacuum filtration and washed with water. The yield was 20.3 g (86.6%). ¹H NMR (DMSO-*d*₆): δ 9.79 (s, 1H), 7.75 (d, 2H), 7.65 (d, 2H), 4.47 (s, 2H).

Table 1			
NMRP of 5	and 9	in various	conditions ^a .

Polymer Monomer (M) Initiator (I) mol ratio [M]/[I] Time [h] Yield [%] M_n^b [kDa] $M_{\rm w}^{\rm b}$ [kDa] PDI^b m:n^c P1 10 6 1.5 65 2.5 3.1 1.25 9 9 10 59 29 P2 6 2 3.4 1.14 **P**3 9 10 6 3 53 3.0 3.4 1.15 _ P4 9 10 25 37 1 4.6 6.1 1.33 P5 5 10 25 6 38 2.0 2.7 1.35 B1 5 **P1** 0.87 24 19 2.9 3.7 1.27 42:58 **B2** 5 P2 2 24 40 6.1 8.0 1.30 67:33 4.5 P2 **B3** 5 24 51 7.3 9.2 1.26 80:20 B4 P3 24 26 8.3 1.54 5 5 5.4 84:16

^a Polymerizations were carried out in *o*-dichlorobenzene (3 mol/L) at 130 °C under nitrogen atmosphere.

^b Determined by GPC eluted with chloroform using polystyrene standard.

^c Molar ratio of **5** to **9** estimated from ¹H NMR.

2.8. Synthesis of 1-(4-t-butylbenzoyl)-2-(4-bromobenzoyl) hvdrazine (**7**)

To a two-necked flask equipped with a stopcock and an additional funnel were added **6** (20.0 g, 93.0 mmol) and pyridine (250 mL) under nitrogen atmosphere. The solution of *t*-butylbenzoyl chloride (18.3 g, 93.0 mmol) in pyridine (100 mL) was added dropwise at 0 °C, then the mixture was stirred for 3 h. After an additional stirring was continued for 3 h at room temperature, water was added to precipitate the product. The white solid was filtered and washed with water. The yield was 33.1 g (94.8%). ¹H NMR (DMSO-*d*₆): δ 10.41 (s, 2H), 7.86 (d, 4H), 7.72 (d, 2H), 7.52 (d, 2H), 1.31 (s, 9H).

2.9. Synthesis of 2-(4-bromophenyl)-5-(4-t-butylphenyl)-1,3,4-oxadiazole (**8**)

To a two-necked flask equipped with a stopcock and a condenser were added **7** (33.0 g, 87.9 mmol) and phosphorous oxychloride (200 mL) under nitrogen atmosphere, and stirred at 100 °C for 20 h. After cooling down to room temperature, excess phosphorous oxychloride was removed under vacuum. Water was added to the residue, and the precipitate was filtered and washed with water. The white crystal was obtained by recrystallization from ethanol. The yield was 20.0 g (63.7%). ¹H NMR (DMSO-*d*₆): δ 8.02 (d, 4H), 7.80 (d, 2H), 7.62 (d, 2H), 1.33 (s, 9H).

2.10. Synthesis of 2-(4-t-butylphenyl)-5-(4-vinylbiphenyl-4'-yl)-1,3,4-oxadiazole (**9**)

To a two-necked flask equipped with a condenser were added **8** (4.65 g, 13.0 mmol), 4-vinylphenylboronic acid (2.00 g, 13.5 mmol), tetrakis(triphenylphosphine)palladium(0) (0.312 g, 0.27 mmol), and dry THF (15.0 mL) under nitrogen. After the solution of potassium carbonate (3.74 g, 27.1 mmol) in oxygen-free water (13.5 mL) was added, the mixture was stirred at 70 °C for 24 h. The resulting mixture was extracted with chloroform, and the organic layer was dried with magnesium sulfate and concentrated by rotary evaporator. The crude product was purified by silica gel column chromatography eluted with chloroform/ethyl acetate (95/5) followed by recrystallization from methanol to yield the white crystal. The yield was 2.99 g (60.5%). ¹H NMR (CDCl₃): δ 8.21 (d, 2H), 8.09 (d, 2H), 7.77 (d, 2H), 7.64 (d, 2H), 7.57 (d, 2H), 7.53 (d, 2H), 6.78 (dd, 1H), 5.84 (d, 1H), 5.32 (d, 1H), 1.38 (s, 9H).

2.11. General procedure for syntheses of macroinitiators (P1-P4)

To a glass tube equipped with a stopcock were added **9** and **10** in the stated ratio under nitrogen atmosphere. After fresh dry

 Table 2

 Random copolymerizations of 5 and 9^a.

Polymer	Feed ratio [5]:[9]	Yield [%]	$M_{\rm n}{}^{\rm b}$ [kDa]	$M_{ m w}{}^{ m b}$ [kDa]	PDI ^b	m:n ^c
R1	20:80	39	37	101	2.71	15:85
R2	50:50	40	52	122	2.44	44:56
R3	67:33	65	12	51	4.13	60:40
R4	83:17	28	11	37	3.34	78:22

 $^{\rm a}$ Polymerizations were carried out in o-dichlorobenzene (1 mol/L) at 80 $^\circ {\rm C}$ for 18 h under nitrogen atmosphere.

^b Determined by GPC eluted with chloroform using polystyrene standard.

^c Molar ratio of **5** to **9** estimated from ¹H NMR.

o-dichlorobenzene was added, the mixture was degassed by freeze–thaw cycles. The tube was sealed under nitrogen, and heated at 130 °C for the stated time. The mixture was cooled down to room temperature, and poured in methanol/acetone (2/1). The polymer was dissolved in chloroform and reprecipitated in methanol/acetone (2/1) repeatedly. The precipitated polymer was collected and dried.

2.12. General procedure for syntheses of block copolymers (B1-B4)

To a glass tube equipped with a stopcock were added macroinitiator (**P1–P4**) and **5** in the stated ratio under nitrogen atmosphere. After fresh dry *o*-dichlorobenzene was added, the mixture was degassed by freeze–thaw cycles. The tube was sealed under nitrogen, and heated at 130 °C for the stated time. The mixture was cooled down to room temperature and poured in acetone. The polymer was dissolved in chloroform and reprecipitated in acetone/THF (9/1) repeatedly. The precipitated polymer was collected and dried.

2.13. General procedure for syntheses of random copolymers (**R1–R4**)

The random copolymers were synthesized from **5** and **9** by a similar method as described in preparation of macroinitiators. As an initiator, 1 mol% of 2,2'-azobis(isobutyronitrile) (AIBN) was used. Purification of the polymers was performed by reprecipitation in methanol several times.

2.14. Device fabrication

Prior to preparation of device, a glass slide with indium tin oxide (ITO) patterns was washed by an alkaline cleaner under sonication



Fig. 1. ¹H NMR spectrum of **B4** measured in CDCl₃ at 400 MHz.

and rinsed with deionized water. The substrate was subsequently washed by 2-propanol under sonication, rinsed with clean 2propanol, and dried with nitrogen. PEDOT:PSS with 30 nm of thickness was spin-coated on the substrate at 2500 rpm for 30 s from the dispersion in water filtered by $0.2 \mu m$ of membrane filter, followed by annealing at 200 °C for 1 h. Polymer layer was laminated on PEDOT:PSS by spin-coating at 300 rpm for 30 s from 1.1.2trichloroethane solution (3 mg/mL) filtered by 0.2 um of membrane filter, and annealed at 120 °C for 1 h under nitrogen atmosphere. On the polymer, 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) with 50 nm thickness was deposited by thermally evaporation in carbon pot at 240 °C under vacuum with a rate of 1.5 Å/s. As a cathode, lithium fluoride with 0.5 nm of thickness followed by aluminum with 100 nm of thickness was deposited on the organic layers at a rate of 0.1 Å/s and a rate of 4.5 Å/s using tantalum and tungsten boats, respectively. Finally, the polymer device was set into a metal can with barium oxide as a drying agent under nitrogen atmosphere, and passivated with an epoxy resin (XNR 5570-B1, Nagase ChemteX Corporation) irradiated by UV light. The typical size of the light emitting area was 4 mm².

2.15. Measurements

¹H and ¹³C NMR spectra were obtained on a JEOL ALPHA400 instrument at 400 and 100 MHz, respectively. Deutrated chloroform was used as a solvent with tetramethylsilane as an internal standard. Number- and weight-average molecular weights (M_n and M_w) were determined by gel permeation chromatography (GPC) analysis with JASCO RI-2031 and UV-970 detectors eluted with chloroform at a flow rate of 0.5 mL/min and calibrated by standard polystyrene samples. Differential scanning calorimetry (DSC) analyses were performed on a Rigaku DSC-8230 under a nitrogen atmosphere at heating or cooling rate of 10 °C/min. The cyclic voltammetry (CV) was measured at room temperature using



Fig. 2. Cyclic voltammograms of B4 film for (a) oxidative and (b) reductive waves vs Ag/AgCl as reference electrode.



Fig. 3. PL spectra of **B4**, **R4**, and polymer blend excited at 313 nm (a) in chloroform solution and (b) in film.

a typical three electrodes system with a working (carbon wire), a reference (Ag/AgCl), and a counter electrode (Pt spiral) under a nitrogen atmosphere at a sweep rate of 10 mV/s. The block copolymer film was fabricated on the carbon electrode from chloroform solution. A 0.1 M solution of tetra-*n*-butylammonium perchlorate in anhydrous acetonitrile was used as an electrolyte. UV–vis and photoluminescent (PL) analyses were conducted on a JASCO V-570 spectrophotometer and a JASCO FP-6500 spectro-fluorometer, respectively.

3. Results and discussion

3.1. Polymer synthesis

As a hole transporting monomer, 2,7-dimethoxy-*N*- (4-vinyl-phenyl)carbazole (**5**) was prepared by 5 steps including the coupling of 2,7-dimethoxycarbazole (**3**) and 4-bromobenzaldehyde followed by the transformation of formyl to vinyl group (Scheme 1).

Table	3
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Energy	levels	of block	copolymers.	

Material	HOMO ^a [eV]	LUMO ^a [eV]	LUMO ^b [eV]	Bandgap ^b [eV]
B1	-5.85	-3.73	2.50	3.35
B2	-5.80	-3.79	-2.45	3.35
B3	-5.80	-3.81	-2.45	3.35
B4	-5.90	-3.79	-2.55	3.35
PBD ^c	-6.3	-	-2.4	3.9
PVK ^d	-5.8	-	-2.2	3.6
Ir(ppy)3 ^d	-5.4	-	-2.4	3.0

^a Estimated by E_{ox}^{o} and E_{red}^{o} determined from cyclic voltammetry.

^b Determined by cutoff wavelength in UV absorption spectrum. ^c Reference [18].

^d Reference [7].

 Table 4

 Device performances based on various polymer systems at 2.7 mA/cm².

Polymer	m:n	Voltage [V]	Luminance [Cd/m ²]	EQE [%]	Power efficiency [lm/W]
R1	15:85	7.90	307	3.20	4.48
R2	44:56	7.04	375	3.98	6.15
R3	60:40	7.20	479	4.97	7.68
B1	42:58	8.00	371	3.50	5.40
B2	67:33	6.20	320	3.39	5.95
B3	80:20	8.00	302	3.12	7.15
B4	84:16	6.78	567	5.88	9.65
R4	78:22	6.83	485	4.98	8.20
blend	84:16	6.82	464	4.88	7.86

Methoxy groups allow the hole transport segment to assemble in the neighborhood of PEDOT/PSS because of their hydrogen bonding with protons of PSS. On the other hand, styryl type monomer containing oxadiazole unit (**9**) was synthesized to construct electron transport segment.

The block copolymers consisting of **5** and **9** were prepared by means of nitroxide mediated radical polymerization (NMRP) using **10** as an initiator (Scheme 2) [17]. Table 1 summarized the results of polymerization in various conditions. Homopolymers of **9** as macroinitiators with narrow polydispersity index (PDI) ranging from 1.14 to 1.33 are obtained in moderate yields. Increasing feed ratio of monomer to initiator ([M]/[I]) slightly broadened PDI for **P4** (1.33). The propagation of second block from macroinitiators was carried out with various concentrations of **5**. Block copolymers with different molar ratios of hole to electron transport segment are obtained. All the block copolymers were purified by fractional reprecipitation in acetone/THF (9/1) to remove unreacted homopolymer. However, PDIs slightly increased compared with those of macroinitiators, especially for high feed ratio as is seen for **B4** (1.54).

Random copolymers were prepared using AIBN for comparison with block copolymers in device performance (Table 2). The polymers with various compositions of **5** and **9** are obtained by changing feed ratios. It is clearly observed that higher amount of electron transport unit tends to be introduced than that of monomer feed ratios because of high reactivity of **9**.

The chemical structures of all the block copolymers were confirmed by ¹H NMR spectra as illustrated in Fig. 1 for **B4**. Signals assignable to methoxy group and *t*-butyl group can be clearly observed at 3.24 and 1.57 ppm, respectively, which prove that both hole and electron transport units are assembled in the polymer structure. The molar ratios of hole to electron transport units in block copolymers (m:n) were calculated from the integral ratio of methoxy group to all aromatic protons.



Fig. 4. Current density and brightness characteristics vs. applied voltage for the devices based on B4, R4, and polymer blend systems.



Fig. 5. External quantum efficiency (EQE) vs. current density for the devices based on B4, R4, and polymer blend systems.

3.2. Optical and electrical properties of polymers

In order to estimate the energy levels of block copolymer, cyclic voltammetry in film was measured for both oxidative and reductive waves. Fig. 2 shows the cyclic voltammogram of B4. Oxidative and reductive peaks can be clearly observed in both operations, which is attributed to simultaneous coexistence of hole and electron transporting moieties in the polymer backbone, namely carbazole and oxadiazole derivatives. The HOMO levels of block copolymers were estimated from standard redox potential (E_{ox}^{o}) values in the oxidation cycle. The energy levels of block copolymers were summarized in Table 3 with those of 2-(4-biphenylyl)-5-(4-t-butylphenyl)-1,3,4-oxadiazole (PBD), poly(vinylcarbazole) (PVK), and *fac*-tris(2-phenylpyridine)iridium (Ir(ppy)₃) as references [7,18]. The HOMO and the lowest unoccupied molecular orbital (LUMO) levels of block copolymers are similar as the HOMO level of PVK and the LUMO level of PBD, respectively. Since the HOMO level lies lower than that of Ir(ppy)₃, energy transfer from the excited polymer backbone to phosphorescent dopant can effectively occurs when the block copolymer is used as matrix for $Ir(ppy)_3$.

PL measurements were carried out for B4, R4, and polymer blend of homopolymers **P1** and **P5** (5:9 = 84:16) in chloroform solution (Fig. 3a) and in film (Fig. 3b). In solution, block copolymer and polymer blend show emission peak around 390 nm derived from carbazole and/or oxadiazole units, whereas only a weak emission at 466 nm is observed in the spectrum of R4. In the case of random copolymer, carbazole and oxadiazole units are settled adjacent to each other, causing an exciplex between them. In the meantime, no significant difference is observed among three samples in film state, showing an emission from exciplex at 445 nm. This finding indicates that, in either block copolymer or polymer blend film, phase-separated structure is not macroscopic one but within the size where hole and electron transport segments can create exciplex because of good miscibility of both segments. In addition, effective energy transfer to phosphorescent dopant $Ir(ppy)_3$ can be expected for all polymers as the maximum emission wavelength at 445 nm matches absorption of Ir(ppy)₃ attributed to metal to ligand charge transfer (MLCT).

3.3. Device evaluation

In order to make an inspect for morphological effect on the OLED performance, electrical phosphorescent properties were studied on the device using **B4**, **R4**, and polymer blend doped by 6 wt% of Ir(ppy)₃. The devices were fabricated as ITO/PEDOT:PSS

(30 nm)/polymer:Ir(ppy)₃ (30 nm)/BCP (50 nm)/LiF (0.5 nm)/Al (100 nm) for all the polymer systems. The polymer blend was prepared by mixing each homopolymers synthesized by NMRP with similar M_n as the segments of block copolymer. As preliminary experiments, the performances of devices utilizing random copolymers with different compositions (R1-R4) were examined as summarized in Table 4. The more the content of hole transport unit increases, the higher the maximum external quantum efficiency (EQE) of the devices becomes. This result indicates that the hole injection is a bottleneck for the device performance using the combination of polymer segments consisted of 5 and 9. Therefore, the ratio of hole transport units to electron transport units of around 80:20 was selected for block (B4), random (R4), and blend copolymers so as to compare the performances at the same composition. The polymer blend composes of P1 and P5 with the molar ratio of 5:9 = 84:16. Fig. 4 illustrates current density and brightness characteristics against applied voltage on the devices. All the polymer systems show similar profiles, and devices using block copolymer and polymer blend pass slightly much current due to modified charge injection by phase-separated structure in the polymer layer, where carbazole units probably gather in neighbor of PEDOT:PSS layer. The EQE at various current densities were determined for all devices as shown in Fig. 5. It is found that block copolymer system exceeds other polymer systems in EQE, reaching up to 6.3%. This resulted from the fact that preventing charges from passing to opposite electrodes as well as improving the injection of charges into the phosphorescent layer was possibly achieved by gradated assembly of hole transport segment next to PEDOT:PSS laver in the block copolymer system. In the blend system, because the similar assembled structure would be constructed as the block copolymer system, high EQE is obtained in smaller current densities. However, thermodynamically unstable structure in the polymer blend caused a decrease in EQE with increasing current, and also resulted in poor life time of device performance (less than a half hour for the brightness half time).

3.4. Conclusion

The block copolymers consisting of carbazole- and oxadiazolecontaining segments as hole and electron transporting units, respectively, were synthesized by NMRP manner. Methoxy groups were introduced to the carbazole monomer, which would lead hole transport segment to the surface of PEDOT:PSS layer by hydrogen bonding with sulfonic acids. It was found by ¹H NMR characterization that block copolymers possessing various ratios of hole to electron transport units were obtained with low polydispersity index. CV measurement of **B4** revealed that the polymer showed bipolar redox behavior with HOMO and LUMO levels at -5.93 eV and -2.54 eV, respectively, enabling hole and electron to be easily injected into the polymer layer. Finally, with $Ir(ppy)_3$ as a phosphorescent dopant, OLED devices were fabricated using block copolymer, random copolymer, and polymer blend for matrix of the emitting layer. From the finding that the block copolymer system overwhelmed the others in EQE, we assumed that a morphology with dimethoxycarbazole units assembled to the surface of PEDOT:PSS played a considerable role for effective recombination of charges as well as sufficient charge injection into the emitting layer.

Appendix. Supplementary data

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.polymer.2009.12.024.

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