

# Synthesis of 5,6-Dihydro[1,10]phenanthroline Derivatives and Their Properties as Hole-Blocking Layer Materials for Phosphorescent Organic Light-Emitting Diodes

Hyo Won Lee,\* Jung-Gi An, Hee-Kyoon Yoon, Hyosook Jang,† Nam Gwang Kim,† and Youngkyu Do†,\*

Department of Chemistry, Chungbuk National University, Cheongju 361-763, Korea. \*E-mail: hwnlee@cbucc.chungbuk.ac.kr

†Department of Chemistry, School of Molecular Science-BK21 and Center for Molecular Design and Synthesis, KAIST, Daejeon 305-701, Korea. \*E-mail: ykdo@kaist.ac.kr

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To develop new hole-blocking materials for phosphorescent organic light-emitting diodes (PhOLEDs), 5,6-dihydro-2,9-diisopropyl-4,7-diphenyl[1,10]phenanthroline (**1**) and 5,6-dihydro-2,9-diisopropyl-4-(4-methoxyphenyl)-7-phenyl[1,10]phenanthroline (**2**) were synthesized. While the absorption spectrum of **1** is very similar to that of **2**, the photoluminescence spectrum of **1** has the feature of the narrower and blue-shifted blue-violet emission at the peak of 356 nm compared to that of **2**. The HOMO and LUMO energy levels of **1** and **2** were estimated from the measurement of cyclic voltammetry, and **1** has the appropriate levels for a hole-blocking layer (HBL). The use of **1** as a HBL in a green PhOLED led to good efficiency of 23.6 cd/A at 4.4 mA/cm<sup>2</sup>.

**Key Words** : BCP derivatives, 5,6-Dihydro-2,9-diisopropyl-4,7-diaryl[1,10]phenanthroline, Hole-blocking materials, Phosphorescent organic light-emitting diode

## Introduction

In recent years, the application of organic light-emitting diode (OLED) has been increasing due to the advantages of self-emission, fast response time, high brightness, and so on.<sup>1</sup> Hence, in particular, the studies on OLED materials and devices have been actively directed toward achieving higher performance, leading to, among others, the use of the phosphorescent materials as emitting materials for OLED (PhOLED).<sup>2</sup> The PhOLED utilizes both singlet and triplet excitons.<sup>3</sup> The longer lifetime and the diffusion length of triplet excitons compared to those of singlet excitons<sup>4</sup> make the PhOLED generally require either the use of an additional hole-blocking layer (HBL) between the emitting layer (EML) and the electron-transporting layer (ETL) or the employment of the electron-transporting layer with hole-blocking ability (HBETL) instead of ETL in the general OLED structure of anode/hole-transporting layer (HTL)/EML/ETL/cathode. The purpose of the use of HBL or HBETL is to increase the electroluminescence (EL) efficiency by confining the recombination of injected holes and electrons and the relaxation of created excitons within the EML.<sup>5,6</sup> To meet such roles, the hole-blocking materials should have HOMO and LUMO energy levels suitable to block hole transport from the EML to the ETL and to pass electrons from the ETL to the EML in addition to the good thermal and electrochemical stability.<sup>7</sup> Currently, the examples of the hole-blocking materials are very limited and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline, known also as bathocuproine (BCP),<sup>5a</sup> and bis(2-methyl-8-quinolinolato)mono(4-phenylphenolato)aluminum (BALq)<sup>8</sup> have been used as the typical materials for the HBL and HBETL of PhOLED, respectively. However, they show several problems such as the low thermal stability and the high

driving voltage. As a part of our efforts in synthesizing new hole-blocking materials, the derivatization of BCP has been attempted. Reported herein are the synthesis of 5,6-dihydro-2,9-diisopropyl-4,7-diphenyl[1,10]phenanthroline (**1**) and 5,6-dihydro-2,9-diisopropyl-4-(4-methoxyphenyl)-7-phenyl[1,10]phenanthroline (**2**), whose structures are shown in Scheme 1, and the accounts of their properties as hole-blocking layer materials in a green-emitting phosphorescent OLED.

## Experimental Section

**General Comments.** Unless otherwise indicated in a specific experiment, all of the chemicals used were reagent grade and no additional purification has been done. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl immediately prior to use. Dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) was distilled from calcium hydride. Thin layer chromatography (TLC) was performed on E. Merk silica gel plates (60F-254) with 0.25 mm thickness. Colorization of spots on TLC plates was performed by heating with acidic *p*-anisaldehyde solution or 7% ethanolic phosphomolybdic acid. Flash column chromatography was performed on E. Merk silica gel (F60, 230-400 mesh).

**General Synthesis of Methyl-1-(4-substituted phenyl)-pent-en-3-ones.** To a solution of benzaldehyde compound (50 mmol) and 3-methylbutan-2-one (13.4 mL, 125 mmol) in ethanol (15 mL) was added 10% aqueous NaOH (1.25 mL) dropwise slowly under the nitrogen atmosphere keeping the inner temperature of the reaction mixture below 30 °C. After stirring at room temperature for 6 h, reaction mixture was acidified to pH 2 with dilute HCl solution. The reaction mixture was extracted with benzene (3 × 30 mL) and the combined extract was dried over anhydrous MgSO<sub>4</sub>,

filtered, and concentrated *in vacuo* to obtain the crude residue. The crude product was eluted with a mixture of Hexane : EtOAc = 10 : 1 on a silica gel column to obtain the product.

**Methyl-1-phenylpent-1-en-3-ones (5).** (7.8 g, 90%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 7.60 (d,  $J = 16.1$  Hz, 1H, ArCH=CH), 7.55 (m, 2H, ArH), 7.55 (m, 3H, ArH), 6.81 (d,  $J = 16.0$  Hz, 1H, ArCH=CH), 2.92 (m, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.17 (d,  $J = 6.9$  Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>); IR ( $\nu_{\text{max}}$ , KBr): 2967, 1687, 1663, 1612, 1450, 1205, 1055  $\text{cm}^{-1}$ .

**4-Methyl-1-(4-methoxyphenyl)pent-1-en-3-one (6).** (8.3 g, 81%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 7.54 (d,  $J = 16.0$  Hz, 1H, ArCH=CH), 7.48 (d,  $J = 8.8$  Hz, 2H, ArH), 6.87 (d,  $J = 8.8$  Hz, 2H, ArH), 6.67 (d,  $J = 15.9$  Hz, 1H, ArCH=CH), 3.79 (s, 3H, OCH<sub>3</sub>), 2.91-2.86 (m, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.10 (d,  $J = 6.9$  Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>); IR ( $\nu_{\text{max}}$ , neat): 2968, 1684, 1658, 1598, 1464, 1254, 1174  $\text{cm}^{-1}$ .

**1-Cyclohexenyloxytrimethylsilane (7).** To a solution of diisopropylamine (6.10 g, 61.1 mmol) in THF (30 mL) at 0 °C under the nitrogen atmosphere was added *n*-BuLi (2.5 M in hexane 24 mL) dropwise *via* syringe and the reaction mixture was stirred for 30 min. Then the reaction mixture of LDA was cooled to -78 °C and cyclohexanone (5.00 g, 50.9 mmol) was added. After stirring for 30 min, TMSCl (60 mmol) was added. The resulting reaction mixture was concentrated *in vacuo*. The residue was dissolved in hexane, filtered through a pad of Celite 545, concentrated under the reduced pressure to obtain crude product as a pale yellow liquid (9.9 g, 95%).

**2-[4-Methyl-3-oxo-1-(4-phenyl)pentyl]cyclohexanone (8).** To a solution of ketone **5** (2.87 mmol) in  $\text{CH}_2\text{Cl}_2$  (5 mL) in a two-necked round bottomed flask equipped with an additional funnel at -40 °C under nitrogen atmosphere was added  $\text{TiCl}_4$  (315  $\mu\text{L}$ , 2.87 mmol) dropwise. After stirring for 5 min a solution of 1-cyclohexenyloxytrimethylsilane **7** (3.45 mmol) in  $\text{CH}_2\text{Cl}_2$  (2 mL) was added to the reaction solution for 30 min. After additional stirring for 30 min, the temperature of the reaction mixture was raised to room temperature and water was added to quench the reaction. The reaction mixture was extracted with ether (3  $\times$  10 mL). The combined extracts were dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, concentrated *in vacuo*. The residue was chromatographed on a short column of silica gel eluting with hexane : ethyl acetate = 15 : 1 to obtain crude 1,5-diketone **8**, which was used for the next step without further purification (594 mg, 76%).

**2-Isopropyl-4-(4-phenyl)-5,6,7,8-tetrahydroquinoline (9).** To a solution of 1,5-diketone **8** (0.73 mmol) in acetic acid (5 mL) was added ammonium acetate (168 mg, 2.18 mmol). The resulting solution was refluxed for 2 h. Then the reaction mixture was cooled to 0 °C and neutralized with 20% NaOH solution. The reaction mixture was extracted with  $\text{CH}_2\text{Cl}_2$  (3  $\times$  10 mL) and combined extracts were dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (Hexane : Ethyl acetate = 7 : 1) to furnish tetrahydroquinoline product **9** as a solid (128 mg,

70%). mp: 53.5-55 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 7.46-7.38 (m, 3H, ArH), 7.31-7.28 (m, 2H, ArH), 6.87 (s, 1H, ArH), 3.09-3.00 (m, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.98 (t,  $J = 6.5$  Hz, 2H, ArCH<sub>2</sub>CH<sub>2</sub>), 2.59 (t,  $J = 6.3$  Hz, 2H, ArCH<sub>2</sub>CH<sub>2</sub>), 1.94-1.86 (m, 2H, ArCH<sub>2</sub>CH<sub>2</sub>), 1.75-1.67 (m, 2H, ArCH<sub>2</sub>CH<sub>2</sub>), 1.30 (d,  $J = 6.9$  Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 163.8, 156.3, 149.8, 139.8, 128.3, 128.0, 127.3, 126.8, 118.0, 36.0, 33.0, 27.0, 23.0, 22.9, 22.7; IR ( $\nu_{\text{max}}$ , KBr): 2963, 1585, 1545, 1445, 1375, 1086  $\text{cm}^{-1}$ .

**8-Benzylidenyl-2-isopropyl-4-phenyl-5,6,7,8-tetrahydroquinoline (10).** A solution of **9** (5.0 g, 19.9 mmol) and benzaldehyde (2.62 mL, 25.6 mmol) in acetic anhydride (20 mL) was refluxed at 170 °C for 14 h under nitrogen atmosphere. After cooling the reaction mixture was neutralized with aqueous 10% NaOH solution. The reaction mixture was extracted with  $\text{CH}_2\text{Cl}_2$  (3  $\times$  30 mL). The combined extracts were dried over anhydrous  $\text{MgSO}_4$ , filtered and concentrated *in vacuo*. The residue was separated on a silica gel column (hexane : ethyl acetate = 15 : 1) to obtain product as a yellow syrup **10**. (3.9 g, 58%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 8.08 (s, 1H, ArCH=CH), 7.39-7.17 (m, 10H, ArH), 6.87 (s, 1H, ArH), 3.05-2.98 (m, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.85-2.81 (m, 2H, ArCH<sub>2</sub>CH<sub>2</sub>), 2.62 (t,  $J = 6.0$  Hz, 2H, CCH<sub>2</sub>CH<sub>2</sub>), 1.70-1.62 (m, 2H, ArCH<sub>2</sub>CH<sub>2</sub>), 1.29 (d,  $J = 6.9$  Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 163.8, 151.7, 149.8, 139.8, 138.2, 136.2, 129.6, 128.6, 128.1, 127.9, 127.5, 127.4, 127.1, 126.4, 119.9, 36.1, 28.0, 27.7, 23.0, 22.6; IR ( $\nu_{\text{max}}$ , KBr): 3054, 2960, 1581, 1540, 1494, 1389, 1240  $\text{cm}^{-1}$ .

**2-Isopropyl-4-phenyl-6,7-dihydro-5H-quinolin-8-one (11).** To a solution of compound **10** (600 mg, 1.77 mmol) in a mixture of  $\text{CH}_2\text{Cl}_2$  : methanol = 1 : 1 (20 mL) at -78 °C was passed ozone until the solution turned to blue. Then, the reaction flask was flushed with nitrogen gas and dimethyl sulfide (439 mg, 7.07 mol) was added to the reaction mixture. After stirring for 1 h at room temperature, the reaction mixture was extracted with  $\text{CH}_2\text{Cl}_2$  (3  $\times$  10 mL). The combined extracts were dried over anhydrous  $\text{MgSO}_4$ , filtered, and concentrated *in vacuo*. The residue was separated on a column of silica gel eluting with hexane : ethyl acetate = 4 : 1 to obtain the product as a white solid **11** (421 mg, 90%). mp: 96.6-97.5 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 7.50-7.43 (m, 3H, ArH), 7.33 (d,  $J = 7.1$ , 2H, ArH), 7.26 (s, 1H, ArH), 3.32-3.26 (m, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.88 (t,  $J = 5.9$  Hz, 2H, COCH<sub>2</sub>CH<sub>2</sub>), 2.80 (t,  $J = 6.5$  Hz, 2H, ArCH<sub>2</sub>CH<sub>2</sub>), 2.09-2.05 (m, 2H, ArCH<sub>2</sub>CH<sub>2</sub>), 1.33 (d,  $J = 6.9$  Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 197.3, 166.6, 151.3, 148.0, 138.6, 136.5, 128.9, 128.7, 124.5, 40.0, 36.7, 27.6, 23.1, 23.0; IR ( $\nu_{\text{max}}$ , KBr): 3061, 2965, 1701, 1586, 1495, 1302, 1161, 1036  $\text{cm}^{-1}$ .

**2,9-Diisopropyl-4-phenyl-7-(4-substitutedphenyl)-5,6-dihydro[1,10]phenanthroline.** To a stirred slurry of sodium hydride (21.6 mg, 0.79 mmol) in THF (5 mL) at 0 °C was added solution of **11** (200 mg, 0.75 mmol) in THF (2 mL) under nitrogen atmosphere. Then ketone **5** or **6** (0.79 mmol) in THF (2 mL) was added dropwise to the reaction mixture and stirring was continued for 10 h at room temperature.

Reaction was quenched by adding saturated aqueous  $\text{NH}_4\text{Cl}$  solution (5 mL) to the reaction mixture. The reaction mixture was extracted with ethyl acetate ( $3 \times 10$  mL). The combined extracts were dried over anhydrous  $\text{MgSO}_4$ , filtered and concentrated *in vacuo*. The residue was filtered through short silica gel column (hexane : ethyl acetate = 7 : 1) to obtain crude 1,5-diketone product, which was used for the next step without further purification. **12** (228 mg, 83%), **13** (278 mg, 75%). To a stirred solution of diketone **12** or **13** (0.4 mmol) in acetic acid (10 mL) was added ammonium acetate (100 mg, 1.3 mmol). The reaction mixture was refluxed for 3 h. After cooling the reaction mixture was neutralized with aqueous 20% NaOH solution. The reaction mixture was extracted with ethyl acetate ( $3 \times 5$  mL). The combined extracts were dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated under reduced pressure. The residue was separated on a column of silica gel eluting with hexane : ethyl acetate = 4 : 1 to get 5,6-dihydro-[1,10]phenanthroline as a white solid.

**2,9-Diisopropyl-4,7-diphenyl-5,6-dihydro-[1,10]phenanthroline (1)**. (124 mg, 74%); mp: 182-184 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 7.48-7.31 (m, 5H, ArH), 7.14 (s, 1H, ArH), 3.41-3.32 (m, 2H,  $\text{CH}(\text{CH}_3)_2$ ), 2.75 (s, 2H,  $\text{ArCH}_2\text{CH}_2$ ), 1.40 (d,  $J = 7.1$  Hz, 6H,  $\text{CH}(\text{CH}_3)_2$ );  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 164.8, 150.9, 147.4, 138.2, 127.9, 127.7, 127.2, 126.8, 119.5, 35.3, 23.9, 21.9; IR ( $\nu_{\text{max}}$ , KBr): 3051, 2955, 1579, 1548, 1495, 1225, 1058  $\text{cm}^{-1}$ . HRMS ( $m/z$ ): Calcd for  $\text{C}_{30}\text{H}_{30}\text{N}_2$ , 418.2409; found, 418.2408.

**2,9-Diisopropyl-4-phenyl-7-(4-methoxyphenyl)-5,6-dihydro-[1,10]phenanthroline (2)**. (104 mg, 54%); mp: 67-71 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 7.46-7.34 (m, 5H, ArH), 7.28 (d,  $J = 8.7$ , 2H, ArH), 7.15 (s, 1H, ArH), 7.14 (s, 1H, ArH), 6.98 (d,  $J = 8.7$ , 2H, ArH), 3.85 (s, 3H,  $\text{OCH}_3$ ), 3.41-3.35 (m, 2H,  $\text{CH}(\text{CH}_3)_2$ ), 2.80-2.75 (m, 4H,  $\text{ArCH}_2\text{CH}_2\text{Ar}$ ), 1.42 (d,  $J = 6.9$  Hz, 12H,  $\text{CH}(\text{CH}_3)_2$ );  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 166.3, 166.2, 159.8, 152.5, 152.4, 148.9, 148.6, 139.7, 131.9, 130.5, 129.5, 129.4, 129.2, 128.8, 128.3, 121.1, 121.0, 114.2, 55.7, 36.8, 25.5, 25.4, 23.4; IR ( $\nu_{\text{max}}$ , KBr): 2958, 1597, 1512, 1248, 1177  $\text{cm}^{-1}$ . HRMS ( $m/z$ ): Calcd for  $\text{C}_{31}\text{H}_{32}\text{N}_2\text{O}$ , 448.2515; found, 448.2516.

**Instrumentation.** Melting points were determined on either Electrothermal AZ9003 NK3 or IA 9100 apparatus in capillary tubes and are uncorrected. Infrared (IR) spectra were recorded on a JASCO FT-IR 680 plus spectrometer. NMR spectra were recorded on either Bruker DPX-300 or AMX-500 spectrometer. The  $^1\text{H}$  NMR spectra were measured in  $\text{CDCl}_3$  solution, unless otherwise stated, relative to tetramethylsilane as an internal standard ( $\delta = 0.00$  ppm). For  $^{13}\text{C}$  spectra, the middle peak of  $\text{CDCl}_3$  triplet was used as reference peak ( $\delta = 77.0$  ppm). Elemental analyses were performed on an EA1110-FISONS (CE Instruments) by the Chemical Analysis Laboratory at KAIST. HRMS data were obtained by the Environmental Analysis Laboratory at KAIST on a VG Autospec Ultma. Thermogravimetric analyses (TGA) were carried out under a nitrogen atmosphere at a heating rate of 10 °C/min with Dupont 9900 Analyzer. UV/Vis spectra were obtained on Jasco V-530 spectro-

photometer. PL spectra were recorded on a Spex Fluorog-3 luminescence spectrometer. Cyclic voltammetry was performed on an AUTOLAP/PGSTAT12 with a three-electrode cell in an acetonitrile solution of  $\text{Bu}_4\text{NBF}_4$  (0.10 M) at a scan rate of 50 mV/s. All measurements were carried out at room temperature under ambient atmosphere.

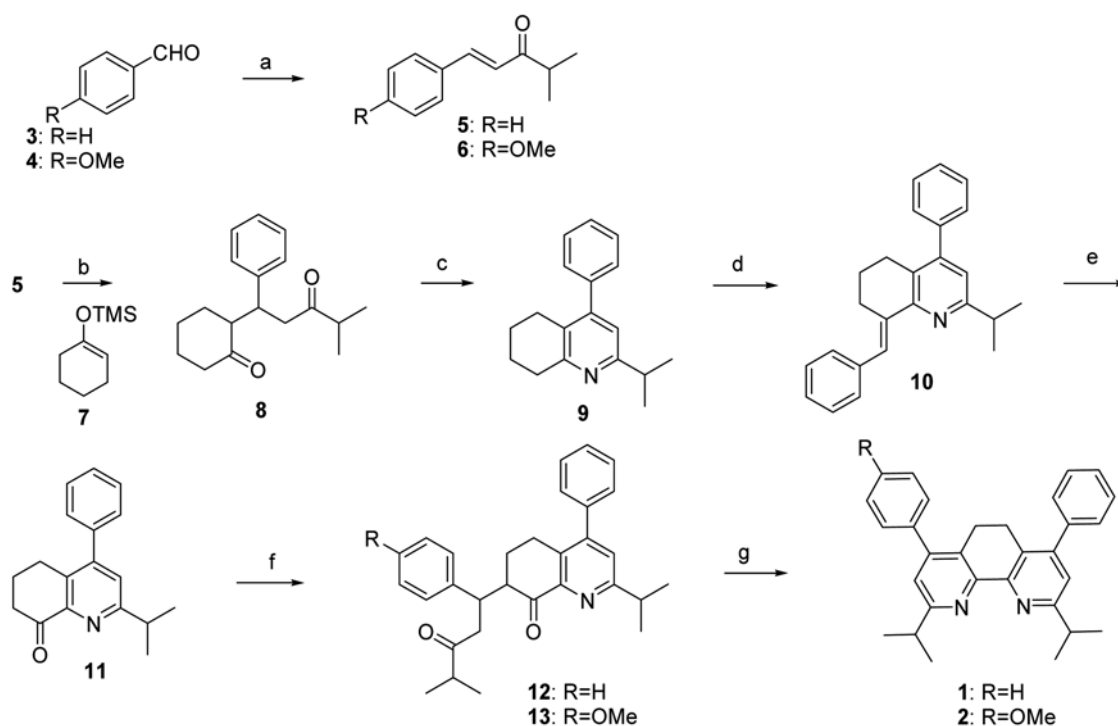
## Results and Discussion

**Synthesis.** The overall synthetic routes are outlined in Scheme 1. In order to prepare a Michael acceptor for 1,5-diketone(**8**), benzaldehyde **3** and *p*-anisaldehyde **4** were condensed with 3-methylbutan-2-one under basic condition to obtain  $\alpha,\beta$ -unsaturated ketones **5** and **6**, respectively. The following Mukaiyama-Michael reaction of **5** with TMS ether **7** of cyclohexenol furnished the desired 1,5-diketone **8**, which upon treatment in a refluxing mixture of  $\text{NH}_4\text{OAc}/\text{HOAc}$  and subsequent neutralization with NaOH afforded pyridine compound **9**. The required ketone **11** was prepared in two steps according to Thummel's method.<sup>9</sup> The treatment of compound **9** with benzaldehyde in acetic anhydride provided  $\alpha$ -benzylidene derivative **10**. And the subsequent ozonolysis provided diketone **11**. The next step along the sequence was the introduction of 1,5-diketone with an aromatic unit from compound **11** for the transformation to the second pyridine unit. Thus Michael addition reaction of **5** and **6** with **11** under basic condition gave corresponding 1,5-diketone **12** and **13**, respectively. Subsequent reaction of **12** and **13** with  $\text{NH}_4\text{OAc}$  in acetic anhydride finally yielded dihydro compound **1** and **2**.

**Properties.** The BCP derivatives **1** and **2** are air-stable in the solid and solution states. Melting points and 5 wt% decomposition temperatures ( $T_{d5}$ ) were investigated to estimate the thermal stability. The  $T_{d5}$  values of **1** and **2** are 250 and 220 °C, respectively and rather low for the use in OLEDs. Contrary to the similar  $T_{d5}$  values, the melting points of **1** and **2** are markedly different as 183 and 70 °C, respectively. It is considered that the introduction of methoxy unit causes the decrease of melting point in **2**.

The absorption and emission spectra of **1** and **2** in  $\text{CHCl}_3$  solution are illustrated in Figure 1 and their summary is listed in Table 1. While the UV-Vis spectra of **1** and **2** are almost alike, the features of photoluminescence (PL) spectra are clearly different in the position of the maximum emission wavelength and in the full-width at the half-maximum (FWHM). The compounds **1** and **2** emit blue-violet and sky-blue fluorescence, respectively, with the relatively low PL efficiency<sup>10</sup> around 0.007-0.014.

Cyclic voltammetry was employed to estimate the HOMO and LUMO energy levels from redox behaviors. All measurements were calibrated using the ferrocene/ferrocenium redox system as a standard.<sup>11</sup> The electrochemical data are summarized in Table 2. Both compounds undergo reversible reduction and irreversible oxidation processes. It is expected that the reversible cathodic reduction raises the probability of stable anion radicals and enables steady injection and transport of electrons in OLEDs. However, **2** seems

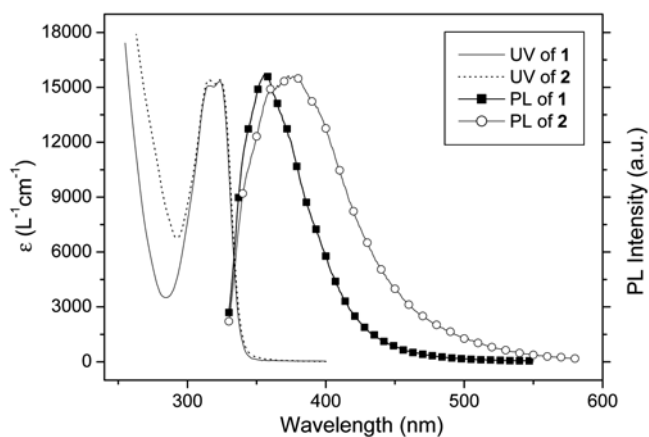


**Scheme 1.** Reagents: a. 3-methylbutan-2-one, 10% NaOH, EtOH, R=H, 90%, R=OMe, 81%; b. **7**, TiCl<sub>4</sub>, CH<sub>2</sub>Cl<sub>2</sub>, -40 °C, 76%; c. NH<sub>4</sub>OAc, reflux, 70%; d. benzaldehyde, Ac<sub>2</sub>O, 170 °C, 58%; e. Oe, -78 °C; Me<sub>2</sub>S, 90%; f. NaH, **5** or **6**, THF, 0 °C -rt, R=H, 83%, R=OMe, 75%; g. NH<sub>4</sub>OAc, AcOH, reflux, R=H, 74%, R=OMe, 54%.

electrochemically unstable because another peak is created and emitting color varies from sky-blue to greenish-blue as the scan number increases. In the anodic scan, each onset of oxidation (*p*-doping) of **1** and **2** appeared at 2.32 and 1.98 V that correspond to HOMO energy levels of -6.72 and -6.38

eV, respectively. The cathodic scan gave each onset reduction (*n*-doping) potential of -0.99 and -0.87 V for **1** and **2** and the LUMO energy levels were calculated at -3.41 and -3.53 eV, respectively.<sup>12</sup> Especially, the HOMO level of **1** is much lower than that of **2** and the energy levels of **1** are similar to those of BCP, a typical hole-blocking material.<sup>5a</sup>

The methoxy-containing compound **2** shows lower thermal and electrochemical stability, narrower bandgap and higher HOMO level as compared with **1**. Therefore, only 1-based green PhOLED was fabricated with the structure of ITO / aromatic amine (650 Å) / NPd (100 Å) / CBP + 8 wt% Ir(ppy)<sub>3</sub> (300 Å) / **1** (50 Å) / Alq<sub>3</sub> (350 Å) / Al (1000 Å) to evaluate hole-blocking layer property of **1** (Figure 2). The EL spectrum of pure Ir(ppy)<sub>3</sub> was observed at 518 nm without exciplex emission. Figure 3 presents voltage versus current and luminance versus current characteristics. The device exhibited EL performance with turn-on voltage of 7.5 V and maximum luminance of 15200 cd/m<sup>2</sup> at 7 mA. The current density dependency of power and luminance efficiency is depicted in Figure 4. The maximum luminance efficiency was 23.6 cd/A at 4.4 mA/cm<sup>2</sup>. The EL study



**Figure 1.** UV-Vis and PL spectra of **1** and **2** in CHCl<sub>3</sub> solution.

**Table 1.** Summary of UV-Vis and PL spectra of **1** and **2** in CHCl<sub>3</sub> solution

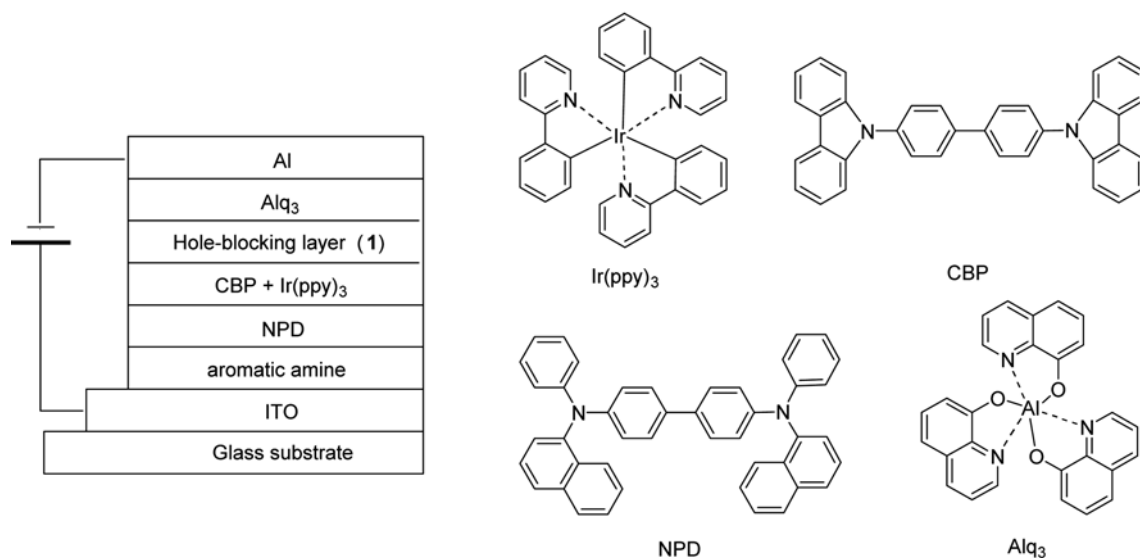
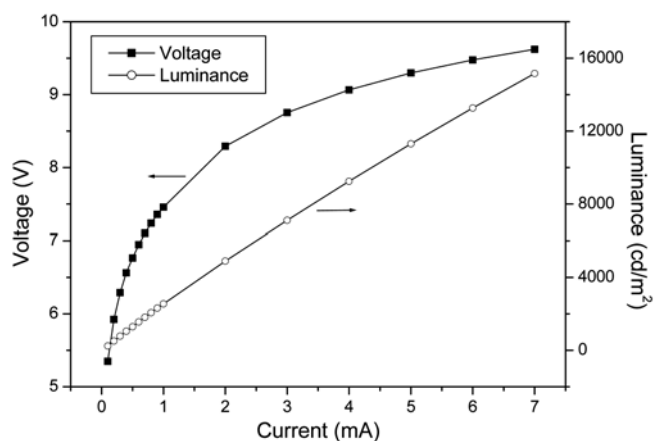
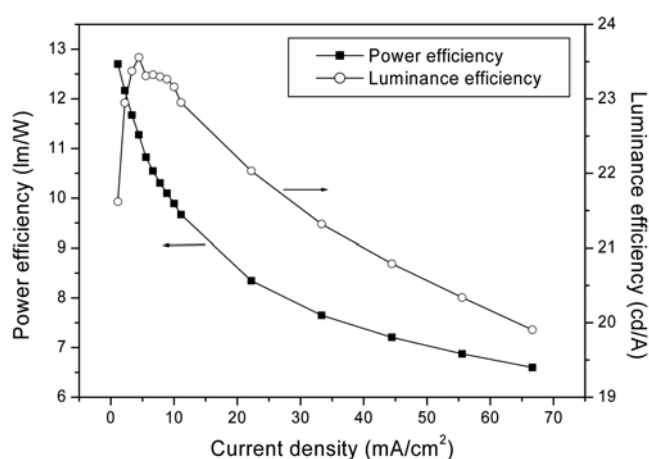
Compound	$\lambda_{\text{abs}} / \text{nm}$ ( $\epsilon / \text{L}^{-1}\text{cm}^{-1}$ )	$E_g / \text{eV}$ (UV/nm) <sup>a</sup>	$\lambda_{\text{em}} / \text{nm}$	FWHM /nm <sup>b</sup>	$\eta_{\text{PL}}^c$
<b>1</b>	316 (15100), 323 (15300)	3.54 (350)	356	54	0.007
<b>2</b>	315 (15400), 324 (15400)	3.36 (369)	375	85	0.014

<sup>a</sup>Optical bandgap was determined from the absorption edge (value in parentheses) of the UV-Vis spectra. <sup>b</sup>Full-width at half-maximum (FWHM) of PL spectra. <sup>c</sup>PL quantum efficiency was determined by using quinine sulfate dihydrate in 1 N H<sub>2</sub>SO<sub>4</sub> solution ( $\eta = 0.55$ ) as a standard.<sup>10</sup>

**Table 2.** Electrochemical data (vs. SCE) and energy levels of **1** and **2** in acetonitrile solution

Compound	<i>p</i> -doping <sup>a</sup> / V			<i>n</i> -doping <sup>a</sup> / V			HOMO <sup>b</sup> /eV	LUMO <sup>b</sup> /eV	E <sub>g</sub> / eV (EChem)
	E <sub>onset</sub>	E <sub>pa</sub>	E <sub>pc</sub>	E <sub>pa</sub>	E <sub>pc</sub>	E <sub>pa</sub>			
<b>1</b>	2.32	–	–3.41	–6.72	–1.60	–0.39	–6.72	–3.41	3.31
<b>2</b>	1.98	–	–3.53	–6.38	–1.30	–0.50	–6.38	–3.53	2.85

<sup>a</sup>E<sub>onset</sub>, E<sub>pa</sub> and E<sub>pc</sub> stand for onset potential, anodic peak potential and cathodic peak potential, respectively. <sup>b</sup>The energy levels were calculated using the empirical equation:  $E = -(E_{\text{onset}} + 4.4)$ .<sup>12</sup>

**Figure 2.** Structures of PhOLED and the used materials.**Figure 3.** V-I-L characteristics of **1**-based PhOLED.**Figure 4.** Device efficiency of **1**-based PhOLED.

shows that the new compound, **1** functions as a good hole-blocking material for the green phosphorescent OLED.

### Conclusion

The synthesis and various properties of two 5,6-dihydro-[1,10]phenanthroline derivatives, **1** and **2** are reported in this paper. The introduction of electron-donating methoxy group in **2** causes broadening of the emission spectrum and lowering of thermal and electrochemical stability compared to **1**. The green phosphorescent organic light-emitting diode

with **1** as a hole-blocking layer showed good luminance efficiency.

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