Synthesis and Application of the Novel Azomethine Metal Complexes for the Organic Electroluminescent Devices

Sung Min Kim, Jin-Soon Kim, Dong-Myung Shin, Young Kwan Kim, and Yunkyoung Ha*

Department of Science, Chemical Engineering, and Research Institute for Science and Technology,
Hong-Ik University, Seoul 121-791, Korea

New azomethine metal complexes were synthesized systematically and characterized. Beryllium, magnesium, or zinc ions were used as a central metal cation and aromatic azomethines (**L1**-**L4**) were employed as a chelating anionic ligand. Emission peaks of the complexes in both solution and solid states were observed mostly at the region of 400-500 nm in the luminescence spectra, where blue light was emitted. Three of them (BeL1 (**I**), ZnL2 (**II**), and ZnL3 (**III**)) were sublimable and thus were applied to the organic light-emitting devices (OLED) as an emitting layer, respectively. The device including the emitting layer of **I** exhibited white emission with the broad luminescence spectral range. The device with the emitting layer of **II** showed blue luminescence with the maximum emission peak at 460 nm. Their ionization potentials, electron affinities, and electrochemical band gaps were investigated with cyclic voltammetry. The electrochemical gaps of 2.98 for **I**, 2.70 for **II**, and 2.63 eV for **III** were found to be consistent with their respective optical band gaps of 3.01, 2.95 and 2.61 eV within an experimental error. The structure of OLED manufactured in this study reveals that these complexes can work as electron transporting materials as well.

Keywords : Azomethine metal complex, Organic electroluminescent devices, Blue and white emission, Band gap.

Introduction

Since the electroluminescence (EL) of a multi-layer device using AlQ_3 as an electron transporting and light-emitting material was reported by Tang *et al*,[1,2] a number of organic electroluminescent materials have been prepared for the light-emitting devices. Among red, green, and blue (RGB) electroluminescent diodes for the full-color display, blue light emitting devices have usually been found to have the lowest efficiencies due to the large band gap of the emitting material.[3] Recently, improved efficiency and luminance in blue EL have been reported with the devices including lithium tetra(hydroxyquinolinolato)boron derivatives,[4] bis(2-methyl-8-quinolinolato) aluminum(III) hydroxide,[5] or alkyl-bridged azomethine zinc complexes, as an emitting layer.[6]

White emission is also necessary for realization of full color in flat displays and for back-lighting in liquid crystal displays. When RGB emitting materials were simultaneously used for the purpose of white emission, difficulties in controlling the respective intensities of RGB peaks led to poor reproducibility and complication of device structures. Light-emitting materials which can produce white emission by themselves are desirable to overcome these problems. A metal chelating complex, bis(2-(2-hydroxyphenyl)benzo-thiazolato)zinc $(Zn(BTZ)_2)$, has been reported to be used as a greenish white emitting material, exhibiting the broad emission spectra.[7]

For the last two years, blue emitting complexes have been synthesized and applied as emitting layers for OLED in our laboratory.[8] As a part of our developments on such light-emitting materials, novel azomethine metal complexes con-

taining Be, Mg, or Zn as a central metal ion chelated with the aromatic azomethine derivatives were prepared in this study. The complexes which could be sublimed among them were investigated as candidates for the light-emitting materials for OLED. In addition, cyclic voltammetry was performed to estimate their HOMO, LUMO, and resulting electro-chemical band gaps for optimization of the device structures. The electrochemical gaps were compared with the UV-Vis absorption spectral edges of the respective complexes.

Experimental Section

General Methods. Reagents were purchased from Aldrich Co. and used without further purification. Solvents used in this study were the reagent grades, purchased from Duksan, Fisher, or Aldrich Co. ^1H NMR spectra were obtained on Varian 200 MHz spectrometer. FAB-Mass spectra were determined on JEOL/JMS-AX505WA in the inter-university center for natural science facilities at Seoul National University. FT-IR spectra were measured on Nicolet Magna-IR 560 spectrometer. UV-vis absorption spectra were measured on Hewlett Packard 8425A spectrometer. The PL and EL spectra were measured on Perkin Elmer LS 50B spectrometer and Keithley 238 electrometer. The current-voltage-luminance characteristics of OLED were measured using the electro-meter with 236 source measurement unit and Minolta Chroma-meter CS 100. The cyclic voltammetry was performed on the vacuum deposited sample on glass with the scan rate of 200 mV/sec. Electroluminescence (EL) spectra were obtained from the device structure of ITO/TPD/an azomethine metal complex/Al.

Table 1. PL Peaks of **L1-L4** in Chloroform

Compound	PL Peak (nm)
L1	414
L2	412
L3	464
L4	416

Table 2. Melting Points of **L1-L4** and Their Complexes

Compound	Melting Point (°C)			
	Ligand itself	Be-Ligand	Zn-Ligand	Mg-Ligand
L1	64-66	110(dec)	>250	204-208
L2	138-140	>250(dec)	>250	>240(dec)
L3	163-165	>250	>250	>250
L4	102-106	>250	>250	>250

Preparation and Characterization of the Azomethine Ligands. Salicylaldehyde (3.2 mL, 30 mmol) dissolved in 50 mL methanol was reacted with 1,3-xylylenediamine (2.0 g, 15 mmol) in 100 mL methanol at room temperature. N,N'-Bis(salicylidene)-1,3-xylylenediamine (**L1**) was precipitated from the reaction mixture. The resulting precipitate was recrystallized in methanol or ethyl acetate. mp 64-66 °C, ^{1}H NMR (CDCl$_3$) δ: 4.91 (s, 4H), 6.9-7.6 (m, 12H), 8.81 (s, 2H), 13.5 (s, 2H), IR ν (C=N): 1633 cm^{-1}.

N,N'-Bis(salicylidene)-1,4-xylylenediamine (**L2**) and N,N'-bis(salicylidene)-1,3-phenylenediamine (**L4**) were synthesized and purified according to the similar method described above. Their PL in chloroform solution was measured and the maximum peaks were listed in Table 1. L2: mp 138-140 °C, ^{1}H NMR (CDCl$_3$) δ: 4.95 (s, 4H), 7.0-7.6 (m, 12H), 8.81 (s, 2H), 13.5 (s, 2H), IR ν (C=N): 1633 cm^{-1}; **L4**: mp 102-106 °C, ^{1}H NMR (CDCl$_3$) δ: 6.8-7.8 (m, 12H), 9.16 (s, 2H), 13.1 (s, 2H), IR ν (C=N): 1622 cm^{-1}.

N,N'-Bis(salicylidene)-1,2-phenylenediamine (**L3**) was purchased from Aldrich Co. and used as received; mp 163-165 °C, IR ν (C=N): 1612 cm^{-1}.

Preparation and Characterization of the Metal Azomethine Complexes. L1 (0.50 g, 1.5 mmol) was dissolved in 50 mL NaOH/methanol and the solution of zinc acetate dihydrate (0.35 g, 1.6 mmol) in methanol was added slowly to yield the azomethine zinc complex, ZnL1, as a precipitate. The precipitate was filtered and washed with deionized water, diluted aqueous solution of NaHCO$_3$, and methanol. The solid was dried in vacuo to yield 0.25 g of ZnL1 (41%). MS (FAB, *m*-NBA) *m*/z 407 (M-H).

The other azomethine metal complexes were also prepared from the reaction of zinc acetate dihydrate, beryllium sulfate tetrahydrate, or magnesium acetate tetrahydrate with an azomethine ligand (**L2-L4**) dissolved in NaOH/methanol, as described for the synthesis of ZnL1. The resulting metal complexes prepared in this study were not very soluble to the common organic solvents and thus metal complex formation was first confirmed by checking their melting points. Melting points of the complexes are summarized in Table 2. Mass spectrometry **BeL1**: MS (FAB, *m*-NBA) *m*/z 352 (M$^+$); **MgL1**: MS (FAB, *m*-NBA) *m*/z 367 (M$^+$); **ZnL2**: MS (FAB, *m*-NBA) *m*/z 407 (M-H), IR ν (C=N) 1618 cm^{-1}; **BeL2**: IR ν (C=N) 1655 cm^{-1}; **ZnL3**: MS (FAB, *m*-NBA) *m*/z 379 (M$^+$), IR ν (C=N) 1614 cm^{-1}; **MgL3**: IR ν (C=N) 1618 cm^{-1}; **ZnL4**: MS (FAB, *m*-NBA) *m*/z 379 (M$^+$), 759 (2M$^+$-H). Further available characterization of the complexes was performed using UV-vis, and photoluminescence (PL). The detailed data were listed, *vide infra*.

Fabrication and Characteristics of OLED. The multi-layer OLED was fabricated by means of a vacuum-deposition method. The ITO coated glass substrates with a sheet resistance of 15 Ω/□ were donated by Samsung Corning Co., Ltd.. The device on the ITO glass consisted of the hole-transport layer (TPD) (400 Å), the emitting layer (an azomethine metal complex) (600 Å), and the metal electrode (Al) (100 Å). The vacuum pressure was maintained at *ca.* 5×10^{-6} torr during the whole sublimation process, and the deposition rate was kept within 1 Å/s. Thickness measurements of various films were carried with the monitor TM-100R by Maxtek, Inc. The emitting area was 3×3 mm^2.

Results and Discussion

Four azomethine ligands (**L1-L4**) containing aromatic spacers were newly prepared (Scheme 1) and characterized with ^{1}H NMR and FT-IR. FT-IR spectra exhibited the stretching frequencies of C=N in the azomethine moiety around 1620 cm^{-1} for each ligand. These stretching frequencies corresponded to the lower limit of typical ν (C=N).[9] ^{1}H NMR of the ligands synthesized in this study revealed the characteristic N=C-*H* signal at 8.81-9.16 ppm. The aromatic signals of the azomethine ligands appeared at 6.8-7.8 ppm with the complicated patterns. The PL peaks of the ligands themselves without metal coordination appeared around 412-464 nm in chloroform solution, as summarized in Table 1.

These ligands were introduced to form the metal complexes, respectively, for understanding the effect of the

Scheme 1. Synthesis of the azomethine ligands and the metal azomethine complexes.

spacers on coordination and luminescence. Be^{2+}, Mg^{2+}, or Zn^{2+} was employed as a central metal ion to investigate metal effect on luminescence and stability. From combination of a metal ion and a chelating azomethine ligand listed above, we were able to obtain 12 complexes in theory. (Scheme 1) The complexes synthesized in this study were found to be insoluble in most of the organic solvents, and these solubility problems inhibited further characterization of the complexes. Melting points of the complexes were found to be above 240 ^{o}C whereas those of the ligands were below 165 ^{o}C. (Table 2) Thus, we presumed that a salt of the complex was formed from the reaction of the ligand with the metal ion. FAB-MS data also supported the formation of the metal complexes, *vide supra*.

Some of the complexes synthesized in this study, however, were found to have rather complicated structures. For example, we found that ZnL4 exists as a dimer, judging from the FAB-MS data. It was likely that formation of a mononuclear complex was not possible due to the rigid conformation of the ligand, **L4**, and a dinuclear structure could be obtained instead. Sublimation is expected to be hindered by these complicated structures, which then make themselves unsuitable for vacuum deposition. Among the metal complexes prepared herein, only BeL1 (**I**), ZnL2 (**II**) and ZnL3 (**III**) were possible to sublime. FAB-MS confirmed the formation of the mononuclear complex in the case of **I-III**, showing their molecular ion peak, respectively.

Modification of the azomethine ligands in the complexes was attempted to improve the solubility of the complexes in the organic solvents and to find the sublimable metal complex substrates. N,N'-bis(salicylidene)-2,3,5,6-tetramethyl-1,4-phenylenediamine (**L5**), 4,4'-(1,3-phenylenediisopropylidene)-bis(N-salicylideneaniline) (**L6**), and 4,4'-(1,4-phenylenediisopropylidene)-bis(N-salicylideneaniline) (**L7**) were prepared and used for the formation of the metal complexes. However, the pre-study on the solubility and sublimability were found to become worse upon the metal complex formation with **L5-L7** than with **L1-L4**.

The solid state fluorescence was measured for all of the complexes synthesized in this study. First of all, they exhibited blue or blue-green emission when exposed upon the light of 365 nm, and thus were prospective candidates for a blue-emitter in OLED. Secondly, their photoluminescent characteristics was investigated. The maximum emission peaks in the resulting PL spectra for the spin-coated films of

Table 3. PL Peaks of **L1**-**L4** and Their Complexes in the Spin-Coated Film

Compound	Peak of Spin-Coated Film (nm)			
	Ligand itself	Be-Ligand	Zn-Ligand	Mg-Ligand
L1	404	410	462	399
L2	no emission	394	425	396
L3	535	406	440	423
L4	no emission	390	503	401

Table 4. PL Peaks of The Metal Complexes of **L1-L4** in Solution

Ligand	Peak in DMSO Solution (nm)		
	Be-Ligand	Zn-Ligand	Mg-Ligand
L1	427	458	463
L2	429	444	468
L3	465	510	453
L4	447	472	456

each complex were listed in Table 3. Spin-coated films were prepared from the dilute DMSO solutions of the complexes followed by evaporation of the solvent. Among the complexes with the same ligand, the magnesium complexes displayed emission at the lowest wavelengths and thus exhibited blue luminescence of the highest energy. On the other hand, the zinc complexes showed emission at the longest wavelengths. It was reported that the emission shifts to longer wavelength as the covalent nature of the metal-ligand bonding (primarily M-N) is increased.[3] Zn^{2+} is known to yield more covalent character than Be^{2+} or Mg^{2+} when complexed with the chelating azomethine ligand. Therefore, our results that the zinc complexes exhibited the lowest energy emission are consistent with the statement previously reported.

The complexes were barely soluble in dimethylsulfoxide (DMSO) and their solution PL spectra were obtained in dilute DMSO solutions. (Table 4) Solution PL data were found to be somewhat different from the spin-coated solid film data, and generally red-shifted. Presumably the solid state film has more intermolecular interaction than the compound in solution and may thus lead to emission at different wavelengths. Compact piling of the solids may even result in self-quenching, as no emission was observed in the solid films of the ligand, **L2** and **L4**. Or this difference may result from some change in intramolecular interactions between the metal center and the ligand in DMSO solution compared to those in solid state. DMSO known to have the relatively high dielectric constant can weaken interactions between the metal ion and the ligand in the complexes.

For the complexes (**I** and **II**) found to be sublimable, vacuum deposited single layer films were made. Their PL peaks appeared at 447, 540 nm for **I**, and 464 nm for **II**. (Table 6) The PL spectra of the vacuum deposited films were found to be somewhat different from those of spin-coated films. At this moment, the reason for these differences was not identified, but it was suspected that the residue of DMSO caught in the spin-coated films might

Table 5. IP, EA and E_g of **I-III**, and Their Optical Band Gaps

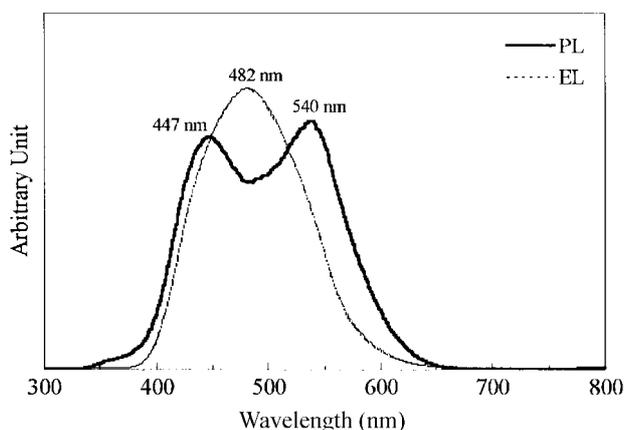| Complex	IP (eV)	EA (eV)	E_g (eV)	UV-vis Edge (nm/eV)
I	5.87	2.89	2.98	412 / 3.01
II	6.00	3.30	2.70	422 / 2.94
III	5.48	2.85	2.63	475 / 2.61

Table 6. Luminescent Characteristics of **I** and **II**

Complex	PL (nm)	EL (nm)	Turn-on Voltage (V)	Maximum Luminance (cd/m^2)
I	447,540	482	11.5	292
II	464	450	8.5	–

interact with the complexes and thus change the PL patterns.

An electrochemical method, cyclic voltammetry, was employed to investigate the ionization potential (IP), the electron affinity (EA), and the resulting electrochemical gaps (E_g) of the complexes. IP and EA of the complexes can be estimated from the extrapolated onsets of their oxidation and reduction potentials, respectively. IP and EA may be regarded as the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of a complex, respectively.[10] It is important to obtain information about HOMO and LUMO of the emitting layer for designing optimized device structures. The electrochemical gap can be measured from the difference between IP and EA values. In other words, E_g should be able to represent the band gap between HOMO and LUMO. The band gap can also be obtained optically either from photo-electron spectroscopy (PES) data or from extrapolated UV-Vis absorption edges. The complexes, **I**, **II**, and **III** were subject to cyclic voltammetry, and their E_g values were measured to be 2.98, 2.70, and 2.63 eV, respectively. The overall IP, EA, and E_g data of each complex were listed in Table 5. From the UV-vis absorption spectra, optical band gaps of **I**, **II**, and **III** were estimated to be 412, 420, and 475 nm, which correspond to 3.01, 2.94, and 2.61 eV, respectively. Therefore, it was concluded that the E_g values were consistent with the respective optical band gaps within an experimental error.

The complexes, **I**, **II**, and **III**, were applied as light-emitters to OLED. The devices were fabricated with the structure of ITO/TPD/an azomethine metal complex/Al. In this structure, ITO and Al electrode were employed as an anode and a cathode, respectively, and TPD was used as a hole transporting layer. The azomethine metal complex (**I-III**) which could sublime was vacuum deposited, forming an
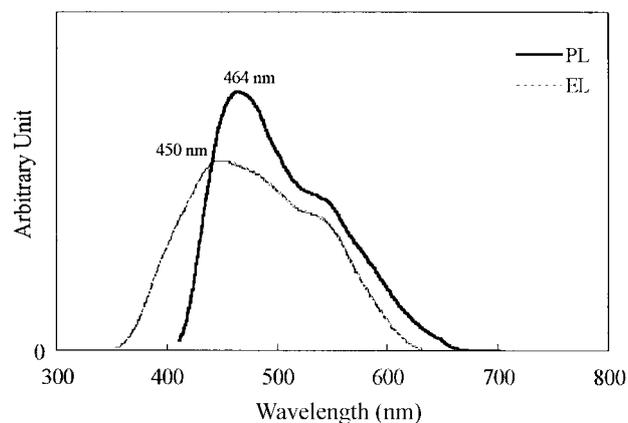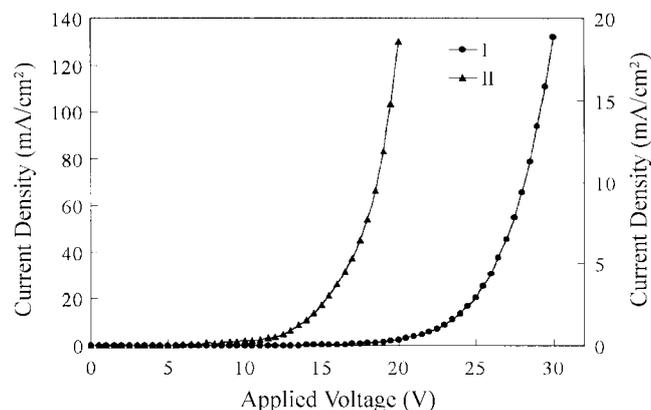
amorphous thin film of the emitting layer.

The EL peak of **I** was found around 482 nm with rather broad range in emission wavelengths while its PL spectra revealed two peaks of 447 and 540 nm. (Figure 1) In fact, the EL peak wavelength of 482 nm was in between the two PL peaks, but the spectral patterns were different from each other. It should be reminded here that PL spectra were obtained with single layer vacuum deposited films while EL spectra were obtained from the double layer structures. Thus, some interaction may occur between TPD and the emitting layer in EL, yielding different PL and EL peaks. A few examples of complexes were reported to show such differences between PL and EL.[6,11]

More intriguing spectral difference between PL and EL was observed with the device containing the emitting layer of **III**. The maximum PL peak was found at 440 nm while the EL maximum was observed at 533 nm. It was inferred in this case that emission at 533 nm was originated from the free ligand isolated by decomposition of **III** during vacuum deposition. The complex, **III**, seemed to be decomposed during fabrication of the device. Therefore, further investigation of the EL device containing **III** was not performed.

The EL and PL spectra of **II** were compared as shown in Figure 2. The maximum PL occurred at 464 nm with a shoulder of 540 nm and the EL peaks were observed at 450

Figure 2. EL *vs*. PL spectra of **II**.

Figure 1. EL *vs*. PL spectra of **I**.

Figure 3. I-V Curves of **I** and **II**.

nm with a shoulder of 545 nm. Though the EL peaks were slightly blue-shifted compared to those of PL in this complex, EL and PL spectra were found to exhibit similar emitting patterns, indicating that the origin of light is attributed to the intrinsic emission from the emitting layer, **II**.

From the structure of the electroluminescent devices manufactured in this study, it was noted that there was no electron transporting layer employed in the device. It indicated that the emitting layer of the metal complexes also played the role of the electron transporting layer. Therefore, the complexes reported herein may find the application as the materials for the electron transporting layers in OLED as well.

The turn-on voltages of **I** and **II** were observed at 11.5 and 8.5 V, respectively. (Figure 3) The overall PL and EL data were listed in Table 6. Maximum luminance of **I** was measured to be 292 cd/m^2. Its broad emission range led to white emission with CIE coordinates $x : 0.250$, $y : 0.295$. White emission by **I** was an encouraging result with respect to development of white emitting materials because such complexes have been rare. A desirable white emitting material should have broad PL spectra with the maximum peak in the green region. In this aspect, **I** can be a prospective candidate for a white light-emitting layer in OLED.

The device containing **II** displayed blue emission for the short operating time but did not survive enough to measure maximum luminance and CIE coordinates. Though the device with the emitting layer **II** has not been attempted to optimize yet, this result suggests a promising future of ZnL2 as a blue emitter. Further studies on the improvement of the device performance are planned in this laboratory. We expect that employment of Li-Al anode instead of Al and/or introduction of the electron transporting layer of AlQ$_3$ may contribute to optimization of the device containing the complexes synthesized herein.

Conclusion

By systematic variation of the spacer groups in the chelating ligand and by introduction of various metal centers in the synthesis of metal azomethine complexes, the effect of spacers and the central metal on luminescence and stability was revealed. Emission colors, luminance characteristics, electrochemical properties, and stability were influenced by the types of metal centers and ligand spacers in the aromatic azomethine metal complexes. It was found that the ligand

conformation had great influence on metal complex formation and sublimation capability. BeL1 (**I**), ZnL2 (**II**), and ZnL3 (**III**) were possible to sublime and thus employed as an emitting layer in OLED. White electroluminescence with the device containing **I** and blue electroluminescence with the device containing **II** were observed. The complex **III** was decomposed during fabrication of the EL device. The electrochemical gaps obtained from the difference between the IP and EA values were consistent with optical band gaps measured from the absorption edge on UV-Vis spectra, giving the information of HOMO, LUMO, and the emission colors of the complexes. We found that the azomethine complexes synthesized herein worked not only as an emitting layer but also as an electron transporting layer, judging from the device structure.

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