Hydroxyphenyl-pyridine Beryllium Complex ($\mathbf{Bepp_2}$) as a Blue Electroluminescent Material

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A novel blue luminescent chelate complex $\mathbf{Bepp_2}$ (**pp** = 2-(2-hydroxyphenyl)pyridine) was synthesized as an electroluminescent material. The single-crystal X-ray diffraction study showed that there are intermolecular $\pi\cdots\pi$ interactions in the solid state of $\mathbf{Bepp_2}$. This structural character can facilitate charge transport ability. The photoluminescence and electroluminescence properties of $\mathbf{Bepp_2}$ were characterized. $\mathbf{Bepp_2}$ exhibits very strong photoluminescence at 440 nm in chloroform solution. Its PL quantum yield is 80% higher than that of Alq_3 in solution. In this paper we report that $\mathbf{Bepp_2}$ can be used as an emitting material to fabricate blue light electroluminescent devices. The devices with the configuration of [ITO/Cu−Pc/TPD/$\mathbf{Bepp_2}$/LiF/Al] show electroluminescent efficiency up to 0.55 lm/W. $\mathbf{Bepp_2}$ shows blue EL emission centered at 450 nm. We also demonstrated that $\mathbf{Bepp_2}$ can be used as host material to prepare orange-red EL devices. For the devices of [ITO/TPD/DCM (2wt %) doped $\mathbf{Bepp_2}$/Al], orange-red color light was observed.

Introduction

The design and fabrication of efficient light emitting devices (LEDs) based on organic materials have been areas of active research due to their possible applications in large area display technology. One of the most fascinating advantages in using these organic materials is a wide selection of emission colors in EL displays attainable through the molecular design of organic materials.[1] There have been extensive studies on organic EL devices using low molecular weight complexes with the aim of achieving high brightness, multicolor emission, and improving the durability and efficiency of devices.[2−13] Low molecular weight metal complexes for use as an emitting layer in organic EL devices include Pt−OEP[13] and Eu(III)[14] complexes which emit red light, tris(8-hydroxyquinolinato)aluminum (Alq_3)[15] and bis(10-hydroxybenzo[*h*]quinolinato)beryllium ($Bebq_2$)[16] which emit green light, $Q_2Al{-}OAr$[7] and azomethine-zinc[17] which emit blue light. Generally, Alq_3 and $Bebq_2$ are considered as the most excellent emitting materials for organic EL devices. The common structural feature of 8-hydroxyquinoline and 10-hydroxybenzo[*h*]quinoline ligands is that the two ligands are composed by hydroxyphenyl moiety and pyridyl moiety. For Alq_3 the highest occupied π orbitals (HOMOS) are located on the hydroxyphenyl side and the lowest unoccupied π^* orbitals (LUMOS) are located on the pyridyl side.[18] The emissions of Alq_3 and $Bebq_2$ originate from the electronic $\pi{-}\pi^*$ transitions within q or bq ligands. The two molecules are typical ligand-centered luminescent complexes. These experimental and theoretical results suggest that it might be possible to develop new organic electroluminescent materials by satisfactory combination of pyridyl and hydroxyphenyl groups through appropriate molecular design and synthesis. To explore this idea we focus our attention on 2-(2-hydroxyphenyl)pyridine (**pp**) system to synthesize electroluminescent chelate complexes. We report here that a novel molecular material, $\mathbf{Bepp_2}$, which functions as a blue-emitting material and host material for organic EL devices.

Results and Discussion

The ligand **pp** was prepared from reaction of 2-bromopyridine with 2-bromoanisole. Ligand **pp** coordinated with Be^{2+} to result in the formation of $\mathbf{Bepp_2}$. The

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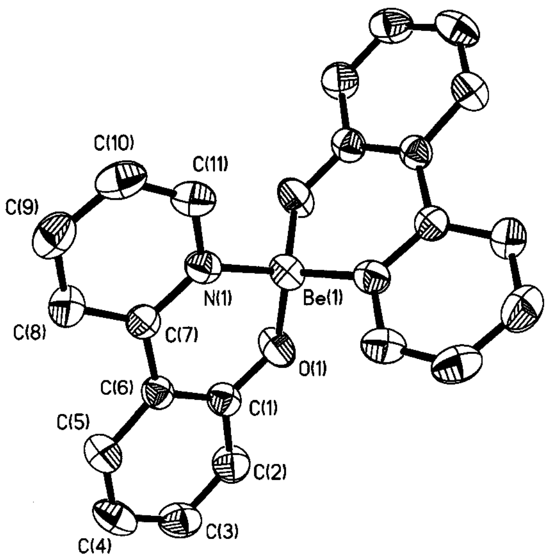

Figure 1. The molecular structure of **Bepp$_2$**.

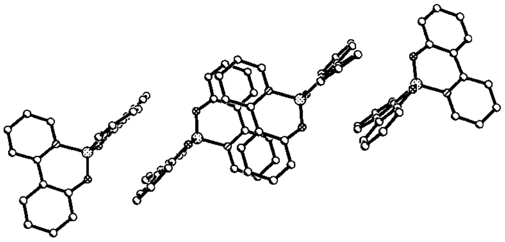

Figure 2. The intermolecular $\pi\cdots\pi$ interactions in the solid state of **Bepp$_2$**.

Table 1. Crystal Data and Structure Refinement for Bepp$_2$

formula	$C_{22}H_{16}BeN_2O_2$
formula weight	349.38
temperature	293(2) K
crystal system	monoclinic
space group	*C*2/*c*
a, Å	14.029(3)
b, Å	10.821(2)
c, Å	12.197(2)
α, deg	90
β, deg	114.84(3).
γ, deg	90.
V, Å^3	1680.3(6),
Z	4
F(000)	728
reflections collected	1939
independent reflections	1483
final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0353$
R indices (all data)	$R1 = 0.0575$

Table 2. Selected Bond Lengths [Å] and Angles [deg] for Bepp$_2$[a]

Be(1)−O(1)	1.564(2)
Be(1)−O(1)#1	1.564(2)
Be(1)−N(1)	1.747(2)
Be(1)−N(1)#1	1.747(2)
O(1)−C(1)	1.319(2)
O(1)−Be(1)−O(1)#1	117.2(2)
O(1)−Be(1)−N(1)	105.19(6)
O(1)#1−Be(1)−N(1)	110.19(6)
O(1)−Be(1)−N(1)#1	110.19(6)
O(1)#1−Be(1)−N(1)#1	105.19(6)

[a] Symmetry transformations used to generate equivalent atoms: #1, $-x, y, -z + {}^1/_2$.

crystal structure of **Bepp$_2$** is presented in Figure 1. The X-ray diffraction study showed that **Bepp$_2$** is a tetrahedral coordination complex. Be^{2+} ion is pseudotetrahedrally coordinated by two bidentate **pp** ligands. The Be−N and Be−O bond distances are 1.747(2) Å and 1.564(2) Å, respectively. The conformation of each **pp** ligand is slightly distortions from planarity. One independent ligand has a torsion angle of 11° between the pyridyl ring and the phenolate ring. After coordination with Be^{2+} ion, the rigidity became stronger in comparison with free ligand, which can reduce the loss of energy via vibrational motions and increasing the emission efficiency, a phenomenon well know to coordination complexes containing luminescent ligand.[19,20] Furthermore, chelation can stabilize the luminescent anion.

X-ray diffraction study revealed that intermolecular $\pi\cdots\pi$ interactions appear in the solid state of **Bepp$_2$**. Each **pp** ligand for a **Bepp$_2$** molecule stacks together with a **pp** ligand in an adjacent **Bepp$_2$** molecule by the $\pi\cdots\pi$ interaction. The interaction continues on to the next molecule, resulting in the formation of a one-dimensional molecular chain (Figure 2). The chains extend in the crystallographic *c* direction. The intermolecular $\pi\cdots\pi$ interaction distance is 3.4 Å. Our earlier report demonstrated that the higher electron mobility of Gaq$_3$ is due to the intermolecular interactions and intermolecular aromatic stacking could offer the charge-transfer pathway.[21] The intermolecular $\pi\cdots\pi$ interactions suggest that **Bepp$_2$** can possess charge transport property, which is an essential property for an electroluminescent material. The crystallographic data of **Bepp$_2$** and its selected bond distances and bond angles are summarized in Tables 1 and 2.

The UV absorption spectrum of **Bepp$_2$** in chloroform solution has maxima at 329 and 361 nm. Upon UV excitation, solution of the complex exhibits intense fluorescence with maximum at 440 nm. The dilute solution relative PL yield of **Bepp$_2$** is 80% higher than that of Alq$_3$. The vapor deposition film of **Bepp$_2$** shows an intensity emission at 450 nm. Note that the PL spectrum in solution is blue-shifted compared with that obtained from solid-state film. This may be attributed to excimer formation between adjacent lumophors in the solid-state film. Figure 3 shows the absorption and PL spectra of **Bepp$_2$** (with excitation at the absorption maximum) obtained from CHCl$_3$ solution together with the PL spectrum recorded for the solid-state film of **Bepp$_2$**. The PL maximum of **Bepp$_2$** is identical with that of **pp** ligand. This suggests that the same types of excitations and energy bands can be involved in the two molecules. In other words, the emission of **Bepp$_2$** originates from the electronic $\pi-\pi^*$ transitions within the **pp** ligand.

First, the test devices were fabricated by vapor deposition of **Bepp$_2$** onto ITO coated glass followed by vapor deposition of aluminum. This gave single-layer devices, which were unstable, although electroluminescence was observed before electrical breakdown. According to the experimental results of Y. Hamada,[16]

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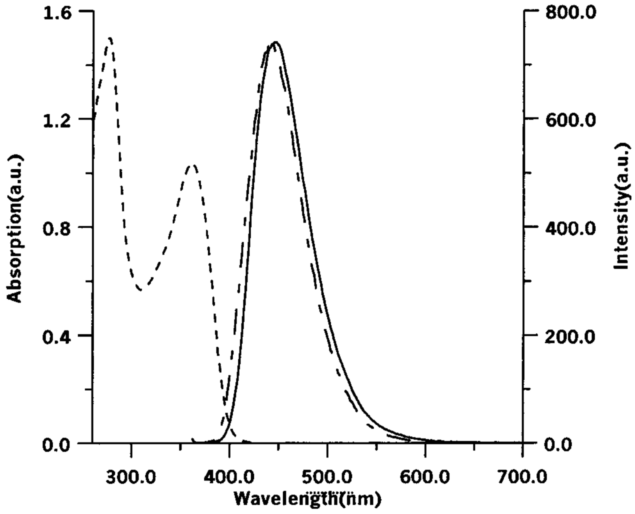

Figure 3. The absorption (···) of **Bepp**$_2$ in chloroform and **PL** (-·-·-) spectra of **Bepp**$_2$ in chloroform and solid film (—).

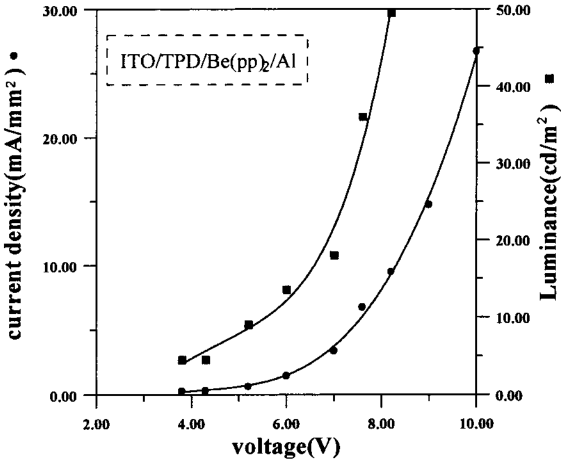

Figure 4. The voltage–current (*V*–*I*) (■) and voltage–luminance (*V*–*L*) (●) characteristics of a device with structure of [ITO/TPD/**Bepp**$_2$/Al].

Bebq$_2$ has good electron transport capability. **Bepp$_2$** and Bebq$_2$ have some similar structural characteristics. We deduced that **Bepp$_2$** should have certain electron transport capability. So we selected **TPD** (*N*,*N*′-diphenyl-*N*,*N*′-bis(3-methylphenyl)(1,1′-biphenyl)-4,4′-diamine) as hole transport material to fabricate double-layer devices. The double-layer EL devices were fabricated by vapor deposition of the organic material onto ITO-coated glass substrate at a deposition rate of 3–5 Å s^{-1} at 5×10^{-6} Torr. Then a layer of aluminum was vacuum deposited onto the organic layer. The structure of the double-layer EL devices is [ITO/**TPD**(500 Å)/**Bepp$_2$**(400 Å)/Al(2000 Å]. The emitting area was 2 × 2 mm^2. All measurements were carried out at room temperature in air. Figure 4 shows typical luminance–voltage (*L*–*V*) and current–voltage (*I*–*V*) curves for a double-layer device. These devices showed a true blue emission under a forward bias. They exhibited differences in maximum luminance (300–400 cd/m^2), maximum luminous efficiency (0.02–0.03 lm/W) and turn on voltage (4–4.5 V). The different EL performances may be attributed to that during the device fabrication each device was located in different position of evaporator, which can result in the difference of deposited film quality for different device. Frequently, the film quality can effect the performance of EL devices. The EL peak wavelength is 450 nm. The half width of the EL spectrum (Figure 5) is 85 nm. The devices exhibited luminance of 45 cd/m^2, EL efficiency of 0.014l m/W and operating voltage of 9.5 V at current density of 100 mA/cm^2. For [ITO/**TPD**(500 Å)/**Bepp$_2$**(400 Å)/Al(2000 Å)] devices, imbalance charge injection is indicated by different turn-on voltages for light (4.5V) and current (3.5V).

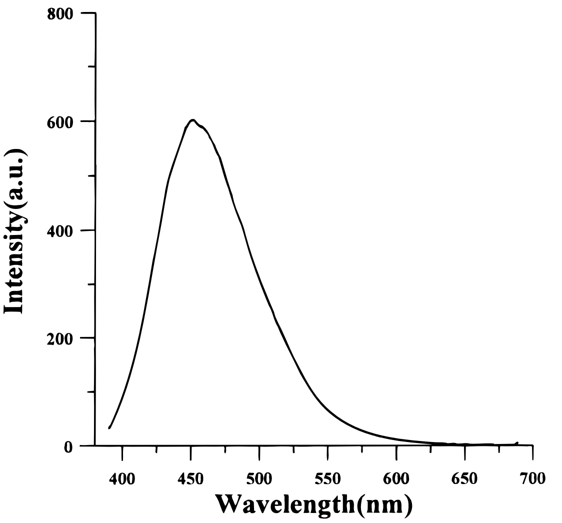

Figure 5. The EL spectrum for a device with structure of [ITO/TPD/**Bepp**$_2$/Al].

It is well-known that the emission of organic electroluminescent devices come from radiative decay of exitons resulting from recombination in of electrons and holes. Balanced injection and transport of electrons and holes is crucial in achieving high quantum efficiency. The facility of charge injection depends on the barriers between the molecular frontier orbitals of the organic material (HOMO for hole injection and LUMO for electron injection) and the work function of the contact electrodes. To achieve efficient electron injection, LiF/Al was employed to fabricate devices with structure of [ITO/TPD(500 Å)/**Bepp$_2$**(400 Å)/LiF(15 Å)/Al(2000 Å)]. When LiF/Al was used as a metal cathode, devices, which have maximum efficiency of 0.26 lm/W and maximum luminance of 800 cd/m^2, show dramatic improvement in the efficiencies compared with the devices with aluminum cathode. The devices with LiF/Al cathode showed luminance of 350 cd/m^2, EL efficiency of 0.09 lm/W and operating voltage of 12V at current density of 100 mA/cm^2. Figure 6 present the luminance–voltage (*L*–*V*) and current–voltage (*I*–*V*) characteristics of [ITO/TPD/**Bepp$_2$**/LiF/Al]. The devices of [ITO/TPD/**Bepp$_2$**/LiF/Al] and that of [ITO/TPD/**Bepp$_2$**/Al] exhibit identical EL spectra. Electroluminescent efficiency was significantly improved by using copper phthalocyanine (Cu–Pc) as a hole-injecting layer and LiF/Al as an electron-injecting layer electrode. The devices with structure of [ITO/Cu–Pc(100 Å)/TPD(500 Å)/**Bepp$_2$** (400 Å)/LiF(15 Å)/Al(2000 Å)] exhibited the maximum luminance of 4000 cd/m^2 and maximum efficiency of 0.55 lm/W. This is due to improved hole injection and electron injection by the modification of the electrode interfaces. The devices with structure of [ITO/Cu–Pc(100 Å)/TPD-(500 Å)/**Bepp$_2$**(400 Å)/LiF(15 Å)/Al(2000 Å)] exhibited luminance of 750 cd/m^2, EL efficiency of 0.21 lm/W and

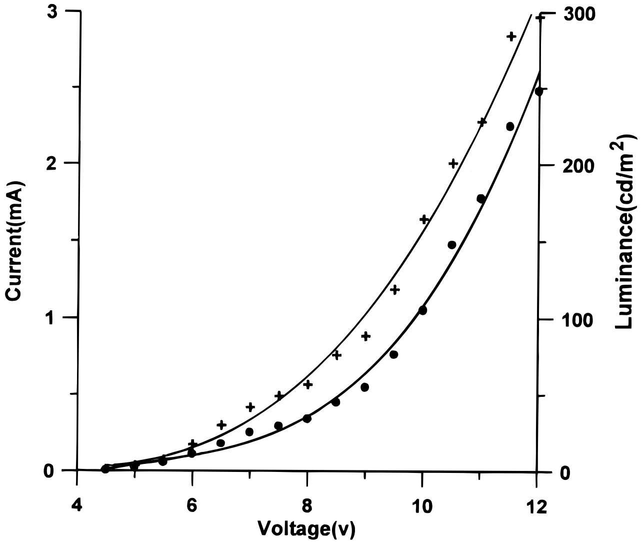

Figure 6. The voltage–current (*V*–*I*) (●) and voltage-luminance (*V*–*L*) (+) characteristics of a device with structure of [ITO/TPD/**Bepp$_2$**/LiF/Al].

operating voltage of 11 V at current density of 100 mA/cm^2.

4-(Dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4-*H*-pyran (DCM) has been used as doped material to obtain red color EL devices.[6] DCM shows strong absorption at wavelength of 450 nm, corresponding to the peak emission of **Bepp$_2$**. This makes DCM a suitable dopant for **Bepp$_2$**-based organic light-emitting devices (LEDs). To study the electroluminescent properties of **Bepp$_2$**:DCM system, organic LEDs were fabricated by vacuum thermal evaporation onto a cleaned glass substrate precoated with conductive, transparent indiums tin oxide (ITO). The test structure is [ITO/TPD (500 Å)/**Bepp$_2$**:DCM (2.5 wt % DCM) (400 Å) /Al (2000 Å)]. The electroluminescent spectra of the devices exhibit only one strong emission at 600 nm, which is due to DCM. This means that energy transfer takes place from **Bepp$_2$** to DCM. The maximum electroluminescent efficiency for the devices with **Bepp$_2$**:DCM dopant film is 0.20 lm/W. The luminance over 1000 cd/m^2 in orange-red region was obtained at a voltage of 15 V. The devices with **Bepp$_2$**:DCM co-deposited layer showed luminance of 452 cd/m^2, EL efficiency of 0.11 lm/W and operating voltage of 12 V at current density of 100 mA/cm^2. The EL spectrum is presented in Figure 7. Higher efficiency EL devices might be obtained with the optimization of device structure. Some experiments are in progress.

Conclusion

In the present study, a novel chelate complex material, **Bepp$_2$**, was synthesized. This chelate complex can be use as a blue emitting material or host material to fabricate organic electroluminescent devices. These results demonstrated that the mixed phenol–pyridine ligands could be used to develop new electroluminescent materials.

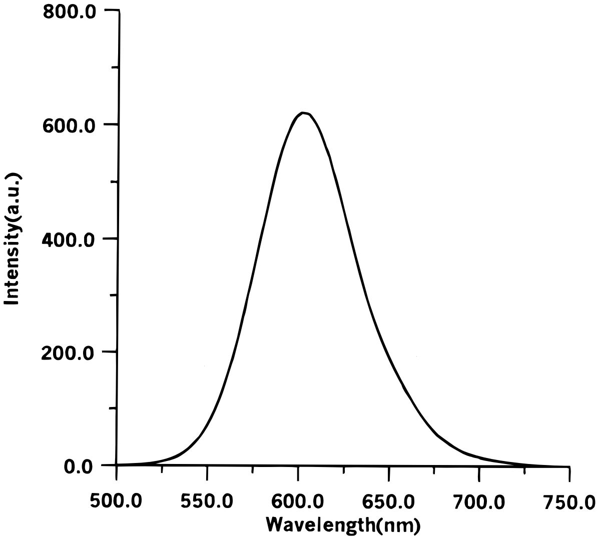

Figure 7. The EL spectrum for the device with structure of [ITO/TPD/**Bepp$_2$**:DCM/Al].

Experimental Section

Bis(2-(2-hydroxyphenyl)-pyridine)beryllum,(Bepp$_2$). The synthesis, structure, and photophysics of **pp** have been described in the literature.[22] **Bepp$_2$** was prepared as following procedure. In a 100-mL round-bottom flask fitted with magnetic stirrer, $BeSO_4 \cdot 5H_2O$ (0.9 g, 5 mmol) and 30 mL of methanol were slowly added to **pp** (1.7 g, 10 mmol) dissolved in 30 mL of methanol. Then the mixed solution was adjusted to pH 12 using NaOH and was stirred for 5 h at room temperature. Colorless solid precipitated from the solution. The solid product was collected by filtration and purified by recrystallization and sublimation methods. EIMS: $m/z = 349$. Anal. Caclcd. for $C_{22}H_{16}N_2O_2Be$: C, 75.6%; H, 4.6%; N, 8.0%. Found: C, 75.2%; H, 4.8%; N, 7.8%.

X-ray Crystallographic Studies. The colorless single crystals of **Bepp$_2$** were obtained by vapor diffusion of diethyl ether in to the solution of **Bepp$_2$** in chloroform at room temperature. Crystallographic data: monoclinic, space group *C*2/*c* with $a = 14.029(3)$ Å, $b = 10.821(2)$ Å, $c = 12.197(2)$ Å, $\beta = 114.84(3)$, $V = 1680.3(6)$ Å,^{3} $Z = 4$. Reflection data were collected on a Siemens R3 four-circle diffractometer using graphite-monochromated Mo Kα radiation and ω scans, giving 1483 unique reflections. The structure was solved by direct methods (SHELXTL VERSION 5) and the structure was refined by least-squares program to a standard discrepancy index $R = 0.0353$ for 1483 reflections with $F > 4\sigma(F)$. Anisotropic thermal parameters were refined for all non-hydrogen atoms.

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Supporting Information Available: Crystallographic data for Bepp2 including a structure analysis report, tables of position parameters, thermal parameters, interatomic distances and angles, observed and calculated structure factors (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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