

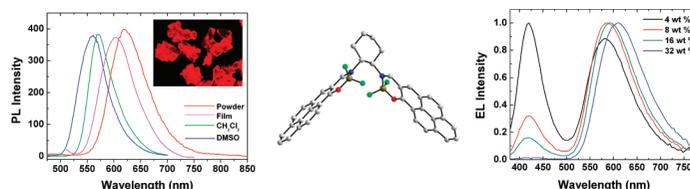
Novel Bi-Nuclear Boron Complex with Pyrene Ligand: Red-Light Emitting as well as Electron Transporting Material in Organic Light-Emitting Diodes

Ying Zhou,^{†,‡} Ji Whan Kim,^{†,§} Min Jung Kim,[‡] Won-Joon Son,^{||} Su Jung Han,[‡] Ha Na Kim,[‡] Seungwu Han,^{||} Youngmee Kim,[‡] Chongmok Lee,[‡] Sung-Jin Kim,[‡] Dong Ha Kim,[‡] Jang-Joo Kim,^{*,§} and Juyoung Yoon^{*,†,⊥}

Department of Chemistry and Division of Nano Sciences (BK21), Ewha Womans University, Seoul 120–750, Korea, Department of Bioinspired Science, Ewha Womans University, Seoul 120–750, Korea, Department of Materials Science and Engineering, OLED center, Seoul National University, Seoul 151–744, Korea, and Department of Materials Science and Engineering, Seoul National University, Seoul 151–744, Korea
jjkim@snu.ac.kr; jyoon@ewha.ac.kr

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ABSTRACT



A novel boron complex bearing a pyrene ligand (CPB) was synthesized and introduced as the first example of a binuclear boron complex in organic light-emitting diodes. In the solid state, CPB2 exhibited strong red emission. In the devices, red emission with Commission International de L'Eclairage (CIE) coordinates of (0.57, 0.42) was obtained by tuning the weight concentration of CPB2. CPB2 behaved as both an emitting and electron transporting material.

Organic fluorine–boron complexes, with BODIPY (dipyrrorboradiazaindacenes) being the best-known example, are well known for their intense fluorescence and tunable emission wavelengths.¹ However, BODIPY and its derivatives exhibit

self-quenching due to the small Stokes shifts and tight packing to reduce their emission efficiency in the solid state, which has severely limited their application potential in organic light-emitting diodes (OLED).² More recently, boron complexes with high solid state emission intensity were reported to have potential as an electron transporting material in OLEDs or dye-sensitized solar cells.³ However, there are few reports of the application of boron complexes as efficient and stable organic red emitters. Therefore, there is a need to

[†] These authors contributed equally to this work.

[‡] Department of Chemistry and Division of Nano Sciences (BK21), Ewha Womans University.

[§] Department of Materials Science and Engineering, OLED center, Seoul National University.

^{||} Department of Materials Science and Engineering, Seoul National University.

[⊥] Department of Bioinspired Science, Ewha Womans University.

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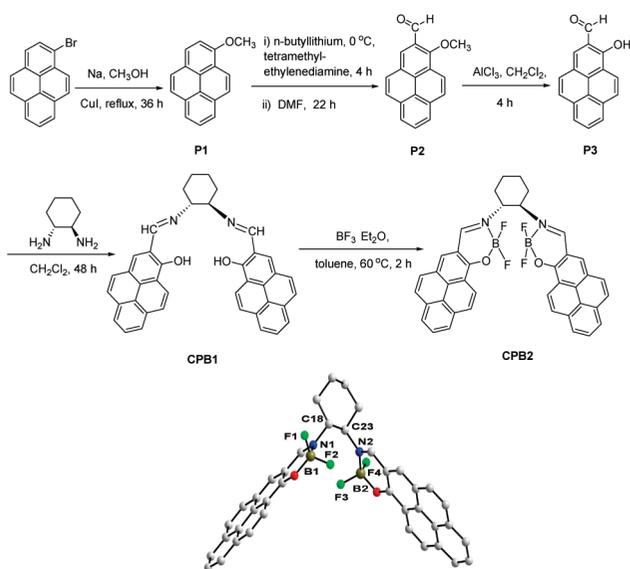
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develop novel boron complexes with a well-designed structure to overcome the weakness of BODIPY and control the optical properties, improve their electron-accepting capability, and apply them successfully to OLEDs.

In the design of the target molecule, this study introduced binuclear boron complex centers, which could not only ensure the strong fluorescence intensity but also form a strong electron-acceptor moiety with a deep LUMO level to facilitate electron transport. To prevent a radiationless transition in the solid state, (1*R*,2*R*)-(–)-1, 2-cyclohexanediamine was introduced as a linker to fix the two pyrene rings in the trans-position with a butterfly shape, which can prevent intimate intermolecular π – π stacking responsible for emission quenching or shifting due to excimer formation.⁴

Scheme 1. Synthetic Route of the Compound **CPB2** and its Crystal Structure



This paper reports the first binuclear boron complex-based red emission OLEDs using pyrene as the fluorophore. Electroluminescence was obtained by doping the complex **CPB2** (bis-[(1-hydroxy-2-pyrenylidene)-(1*R*,2*R*)-cyclohexane-1',2'-diamine]-difluorbor-chelat) into the poly(vinylcarbazole) (PVK). Interestingly, red emission was realized by increasing the doping ratio, and the device containing 32 wt % **CPB2** showed Commission International de L'Éclairage (CIE) coordinates of (0.57, 0.42) (Supporting Information, Figure S6).

Scheme 1 shows the synthetic route of compound **CPB2**. Compounds **P1**–**P3** were synthesized with improved yield by a modification of the reported procedure.⁵ The condensa-

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tion of **P3** with (1*R*,2*R*)-(–)-1, 2-cyclohexanediamine gave **CPB1**, which was rapidly purified by a silicon column owing to its instability, in a high yield of 69%. After BF_3 and Et_2O were added to a **CPB1** solution in toluene, the mixture was stirred under nitrogen for 2 h at 40 °C to obtain **CPB2** in 55% yield. The target compound was purified with a silicon column and recrystallized.

The structure of **CPB2** was characterized by ^1H and ^{13}C NMR spectroscopy and confirmed by X-ray crystallography. As shown in Scheme 1 after coordination, the bonds of C18–N1 (1.486(4) Å) and C23–N2 (1.505(6) Å) were fixed at the trans positions of cyclohexane with a torsion angle of 66.7°, resulting in two pyrene ring planes twisted to each other at 80.4°. The centers of the two boron complexes faced in opposite directions, and the angles of F1–B1–F2 and F3–B2–F4 were 108.3 and 108.2°, respectively. Therefore, a butterfly framework was formed along the ab plane in the crystal cell of **CPB2**.

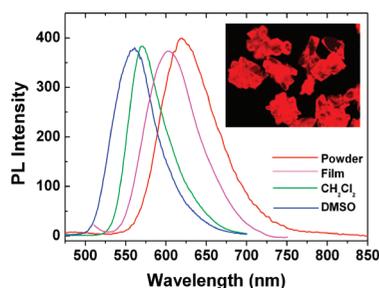


Figure 1. Fluorescent spectra of compound **CPB2** in solution (20 μM in dichloromethane and DMSO) and in solid state (powder and the thin film, which was made by spin-coating on the silicon wafer). (Inset) Solid state fluorescence of the crystal of **CPB2**.

The absorption (Supporting Information, Figure S8) and fluorescence properties of **CPB2** were tested. As shown in Figure 1, compound **CPB2** exhibited an emission band centered at approximately 561 nm in DMSO and 571 nm in dichloromethane. The solid state fluorescence of **CPB2** was characterized using both a thin film spin coated on a silicon wafer and single crystals. The thin film on the silicon wafer was continuous (Supporting Information, Figure S9) and exhibited red-shifted emission centered at 602 nm. The crystals of **CPB2** exhibited strong red fluorescence in the solid state (Figure 1, inset) with a maximum peak at 621 nm, which was red-shifted 19 nm from the thin film maximum emission.

Compared to the emission spectra of the dilute solution, the solid state spectra were red-shifted and slightly broader due to the nonradiative decay caused by intermolecular interactions and inhomogeneous broadening effects. However, it should be noted that the introduction of rigid 1,2-cyclohexanediamine effectively prevented the formation of intermolecular π – π stacking. Therefore, the shape of the fluorescent peaks in the solid state changed very little (fwhm = 62 nm in DMSO; fwhm = 76 nm in film; fwhm = 80 nm

in powder) compared to most BODIPY derivatives, as shown in Figure 1.

The LUMO (lowest unoccupied molecular orbital) energy levels of **CPB2** were determined from the band gaps, which were estimated from the absorption edges, and the HOMO (highest occupied molecular orbital) energy levels, which were estimated from cyclic voltammetry using the Ferrocene/Ferrocene⁺ redox system as a reference. Table 1 summarizes the energy levels in two different solutions. During the anodic scan, the oxidation onset potential of **CPB2** in DMSO was 0.94 V and exhibited an irreversible p-doping process. The LUMO energy levels of **CPB2** were -3.61 eV in CH₂Cl₂ and -3.23 eV in DMSO, respectively, which were both much lower than those of BODIPY and the popular electron transporting material, Alq₃ (-3.0 eV).⁶

Table 1. Electrochemical Potentials and Energy Levels of **CPB2**

compd	condition	HOMO ^a (eV)	LUMO ^b (eV)	E_g^c (eV)
CPB2	CH ₂ Cl ₂	-5.87	-3.61	2.26
	DMSO	-5.70	-3.23	2.47
	Calcd ^d	-5.03	-3.25	1.77

^a Calculated from the oxidation potentials. ^b Calculated from the HOMO energy levels and E_g . ^c Energy band gaps were estimated from the onset wavelengths of the optical absorption. ^d Values come from the quantum chemical calculations.

To obtain more details on the electronic structure, ab initio calculations were performed based on density-functional theory with VASP code.⁷ The projector-augmented wave (PAW) potential was adopted to account for ion-electron interactions, and the generalized gradient approximation (GGA) with the Perdew-Burke Ernzerhof (PBE) functional was used to describe the exchange correlation energy between electrons.

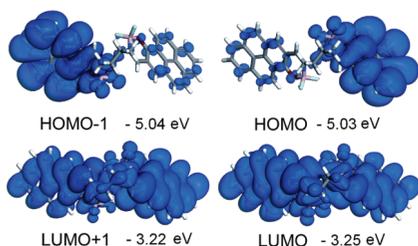


Figure 2. The calculated HOMO, HOMO-1, LUMO and LUMO+1 levels of **CPB2**.

Figure 2 shows the charge densities and HOMO-1, HOMO, LUMO, and LUMO+1 values of the molecule. The charge densities in the HOMOs were localized at either side

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of the pyrene aromatic ring moiety, whereas the LUMO level of **CPB2** was delocalized over the entire molecule. When the molecule was in solution, local anisotropy can lift the degeneracy in the HOMO levels. Therefore, intramolecular charge transfer from one pyrene ring to another pyrene ring and cyclohexanediamine ring was suggested.

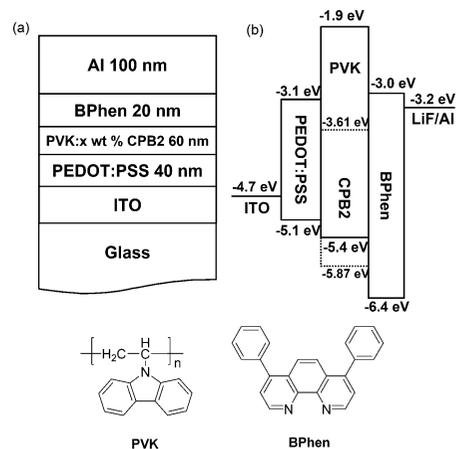


Figure 3. (a) Structures of OLED devices; (b) energy diagram of the devices. (Inset) Chemical structures of the materials used in the devices.

Figure 3a presents the structures of the OLEDs. The hole injection layer of poly(3,4-ethylenedioxythiophene) (PEDOT):poly(styrenesulfonate) (PSS), and emitting layer of PVK doped with **CPB2** were formed by spin-casting, and BPhen, LiF, and Al layers were deposited successively by thermal evaporation. **CPB2** was well dissolved in PVK using cyclopentanone as the solvent to form uniform films. Figure 3b and inset gives the energy levels and molecular structures of PVK and BPhen, respectively.

Figure 4 shows the current density–voltage–luminescence characteristics of the devices with different **CPB2** concentrations. The current density increased dramatically with increasing **CPB2** concentration and became saturated at a **CPB2** content of 16 wt %. A similar trend was observed in the voltage–luminescence curve. The EL intensity increased with increasing **CPB2** concentration to reach the highest luminance at 16 wt %. These characteristics can be interpreted based on the increase of electron current with increasing **CPB2** content in the emitting layer. Since PVK has the high LUMO level (-1.9 eV) and very low electron mobility, injection and transport of electrons in PVK is rather difficult. On the other hand, holes are easily injected and transported in the PVK layer. Therefore, the device containing a low concentration of **CPB2** is expected to be a hole-dominant device with a considerably unbalanced electron–hole concentration resulting in low luminance. With increasing **CPB2** in the emitting layer, however, more electrons are directly injected and transported into the emitting layer through **CPB2** because of its low LUMO levels and close proximity between the **CPB2**, providing more chances for the holes to recombine with electrons on **CPB2** through

Coulomb capture. Therefore, the current density and luminance increase with increasing **CPB2** concentration. Current efficiency of 0.15 cd/A was obtained from the 16 wt % doped device.

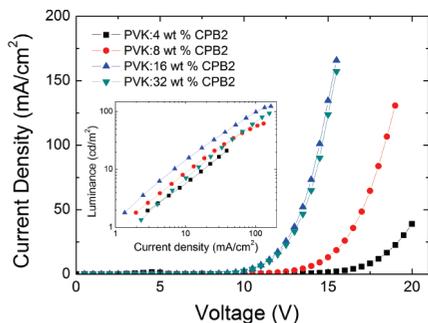


Figure 4. Current density–voltage characteristics of the OLEDs. (Inset) Luminance–current density characteristics of the devices.

This interpretation is supported by the EL spectra shown in Figure 5. The device with low doping concentration of **CPB2** showed large emission from PVK (~ 420 nm). Emission from PVK is reduced with increasing **CPB2** concentration in the emitting layer and most of the emission comes from the **CPB2** when the **CPB2** concentration is 32 wt %. This behavior indicates that more excitons are formed in **CPB2** molecules with increasing **CPB2** concentration, which is consistent with the above explanation. Energy transfer from PVK to **CPB2** is expected to be small because of the relatively small overlap between PVK emission and **CPB2** absorption spectra. In the 32 wt % doped device, orange-red emission with the commission International de L’Eclairage (CIE) coordinates of (0.57, 0.42) was observed.⁸ These results suggest that **CPB2** can behave as both an electron transporting and light emitting material at the same time.

In conclusion, a novel binuclear boron complex with the pyrene ligand was synthesized, and its photophysical,

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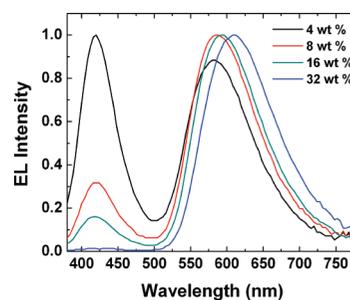


Figure 5. Normalized EL intensity of the OLED devices.

electrochemical, and EL properties were characterized. Complex **CPB2** exhibited strong red-light emission in the solid state. In the polymer light-emitting diodes fabricated with the **CPB2** complex blended with PVK, red emission could be achieved easily by tuning the weight concentration of **CPB2**. **CPB2** can behave as both an emitting and electron transporting material and has the potential for multiapplications in organic light-emitting diodes. Compared to traditional emission and electron transporting materials, further structural optimization enhancing the emission intensity in the solid state is likely to yield more efficient emission materials based on a boron complex. Further study to this end is currently underway.

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Supporting Information Available: Experimental procedures and characterization data of compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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