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 (dipyrroloboradiazaindacenes) being the best-known example, are well known for their intense fluorescence and tunable emission wavelengths. 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). 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. However, there are few reports of the application of boron complexes as efficient and stable organic red emitters. Therefore, there is a need to...
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, (1R,2R)-(−)-1, 2-cyclohexanedi-amine 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

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-(1-hydroxy-2-pyrenylidene)-(1′R,2′R)-cyclohexane-1′,2′-diamine]-difluorobor-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’Eclairage (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 condensation of P3 with (1R,2R)-(−)-1, 2-cyclohexanedi-amine gave CPB1, which was rapidly purified by a silicon column owing to its instability, in a high yield of 69%. After BF3 and Et2O 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 13C 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.

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-cyclohexanedi-amine 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 Ferrocine/Ferrocine\(^*\) 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 CH\(_2\)Cl\(_2\) and \(-3.23\) eV in DMSO, respectively, which were both much lower than those of BODIPY and the popular electron transporting material, Alq\(_3\) (\(-3.0\) eV).\(^6\)

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

<table>
<thead>
<tr>
<th>compd</th>
<th>condition</th>
<th>HOMO(^a) (eV)</th>
<th>LUMO(^b) (eV)</th>
<th>(E_g) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPB2</td>
<td>CH(_2)Cl(_2)</td>
<td>-5.87</td>
<td>-3.61</td>
<td>2.26</td>
</tr>
<tr>
<td></td>
<td>DMSO</td>
<td>-5.70</td>
<td>-3.23</td>
<td>2.47</td>
</tr>
<tr>
<td></td>
<td>Calculated</td>
<td>-5.03</td>
<td>-3.25</td>
<td>1.77</td>
</tr>
</tbody>
</table>

\(^a\) 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 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 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 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\(\rightarrow\)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\(\rightarrow\)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\(\rightarrow\)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

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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.

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, 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.