

Novel Bi-Nuclear Boron Complexes with Pyrene Ligand: Synthesis, Photoluminescence, and Electrochemistry Properties[†]

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Numerous organic molecules and polymers that exhibit electroluminescence (EL) or have electron transporting properties have been reported.¹ Organic fluorine-boron complexes, BODIPY (dipyrro-boradiazaindacenes) being the best-known example, have intense fluorescence and tunable emission wavelengths.² However, BODIPY and its derivatives exhibit self quenching due to the small Stokes shifts and tight packing that reduces their emission efficiency in the solid state, which severely limits their applications to organic light-emitting diodes (OLED).³ More recently, boron complexes with high solid state emission intensity showed potential as an electron transporting material in OLEDs or dye-sensitized solar cells.⁴ However, there are few reports of the application of bi-nuclear boron complexes. 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 bi-nuclear boron complex centers, which not only insure 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, 1,2-phenylenediamine, *p*-xylylenediamine and *m*-xylylenediamine were introduced as linkers to fix the two pyrene rings in the trans-position, which can prevent the intimate intermolecular π - π stacking responsible for emission quenching or shifting due to excimer formation.

Recently, 2-hydroxy pyrene aldehyde (**P3**) was used as a very useful moiety for recognition and OLED material. Owing to presence the aldehyde group, **P3** can be reacted easily with an amine ligand to make a Shift base, which can be reduced further to a benzylic amine group if needed. Furthermore, the phenol moiety on intermediate **P3** can function as an additional binding site for molecular recognition or as the reaction site for a boron group. **P3** is a better building block for chemosensors⁵ than simple pyrene aldehyde because it contains an additional binding site and

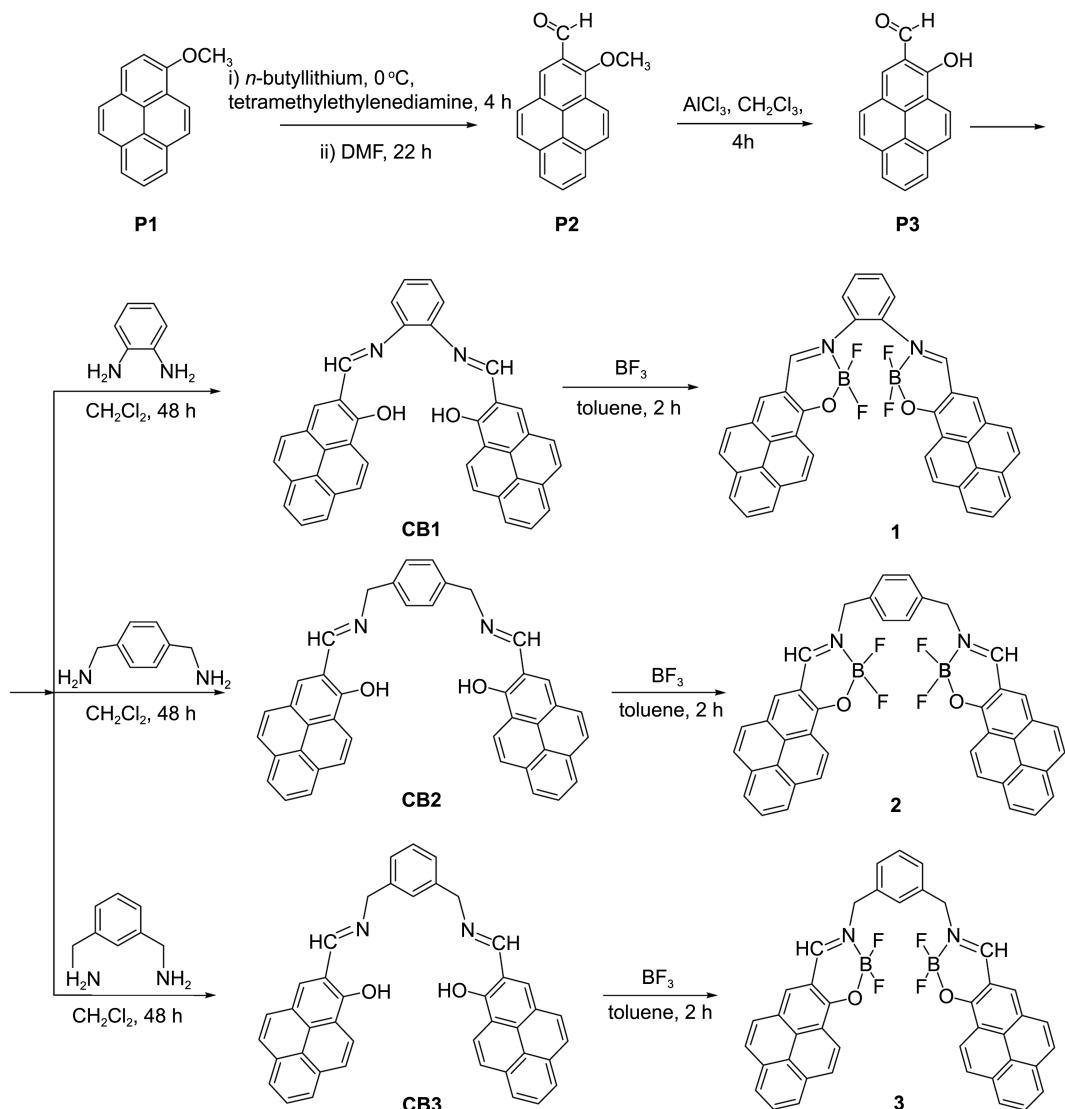
the phenol group also serves as a source of colorimetric changes with ions. A rhodamine derivative bearing a 2-hydroxy pyrene moiety was recently reported to be a ratiometric sensor for Cu²⁺.⁶ Moreover, a hydrazone derivative of 2-hydroxy pyrene and a boron derivative were reported to be a Zn²⁺ sensor⁷ and a new OLED material⁸, respectively.

This paper reports three new bi-nuclear boron complexes **1-3** (Figure 1) that display intense fluorescence in the solution and solid state, low LUMO levels and well-formed thin films. The results highlight their potential as emission materials or electron-transport materials in OLED devices.

The synthesis of compounds **1**, **2** and **3** began from **P3**, which was synthesized according to a reported procedure.⁹ The reaction of **P3** with 1,2-phenylenediamine, *p*-xylylenediamine and *m*-xylylenediamine in CH₂Cl₂ afforded **CB1**, **CB2** and **CB3** in 69%, 60% and 65% yield, respectively (Figure 1). Compound **1** was synthesized by a further reaction of **CB1** with BF₃·Et₂O in toluene at 40 °C in 58 % yield. Compounds **2** and **3** were synthesized in higher yield (60%) by reacting **CB2** and **CB3** with BF₃ using the same procedure used for compound **1**. The detailed synthetic procedures are explained in the experimental section of this paper and the NMR and mass spectra are reported in the supporting information.

The absorption and fluorescence properties of compounds **1-3** were tested. (Supporting Information, Figure S13-S16) As shown in Table 1, compound **1** exhibited an emission band centered at approximately 466 nm in acetonitrile, 472 and 496 nm in dichloromethane and three peaks at 426 nm, 452 nm and 489 nm in DMSO. For compound **2**, similar peaks centered at 564 nm were observed in solutions of DMSO and THF. The solid state fluorescence of compound **2** was characterized using both a thin film spin coated on a silicon wafer and its powder. The thin film on a silicon wafer was continuous (Figure 3) and exhibited emission centered at 583 nm. The powder of compound **2** exhibited orange fluorescence in the solid state with a maximum peak at 607 nm, which was red shifted by 24 nm from thin film maximum emission. In DMSO, dichloromethane and acetonitrile solutions of compound **3**, peaks at 571 nm and 570 nm were observed, respectively.

[†]This paper is dedicated to Professor Eun Lee on the occasion of his honourable retirement.

**Figure 1.** The syntheses of compounds **1**, **2** and **3**.**Table 1.** Optical properties of **1-3**

Cmpd	solvent	UV ($\lambda_{\text{abs}}/\text{nm}$)	FL ($\lambda_{\text{em}}/\text{nm}$)
1	CH ₂ Cl ₂	309	472, 496
	CHCN ₃	302	466
	DMSO	292	426, 452, 489
2	CH ₂ Cl ₂	309	569
	DMSO	305	564
3	CH ₂ Cl ₂	305	571
	CHCN ₃	298	570

In compound **1**, a conjugated system was formed by the introduction of 1,2-phenylenediamine, while in **2** and **3** the non-conjugated systems were formed. Therefore, compared with **2** and **3**, a red-shift in the emission of **1** centered at 645 nm was observed in the solid state. As compounds **2** and **3** have similar structures, both of them exhibited orange-colored fluorescence centered at around 608 nm and 600 nm in solid state, respectively. (Figure 1)

Compared to the emission spectra of the dilute solution, the solid state spectra of compounds **1-3** were red-shifted and slightly broader due to non-radiative decay caused by intermolecular interactions and inhomogeneous broadening effects. However, the introduction of rigid linkers (1, 2-phenylenediamine, *p*-xylylenediamine and *m*-xylylenediamine) prevented the formation of intermolecular π - π stacking. Therefore, the shape of the fluorescent peaks in the solid state changed very little due to the low concentration quenching effect compared to most BODIPY derivatives, as shown in Figure 2.

The electronic states (HOMO/LUMO levels) of compound **1**, **2** and **3** were examined by cyclic voltammetry (CV) (Figure S17). The oxidation CVs of these three compounds were all characterized by an irreversible wave. The ionization potential (IP, HOMO level) of compounds **1**, **2** and **3** were found to be -5.59, -6.02 and -6.02 eV, respectively. Compounds **1-3** also exhibited irreversible reduction waves with the estimated electron affinities (EA, LUMO level) of -3.66 eV, -3.60 eV and -3.59 eV,

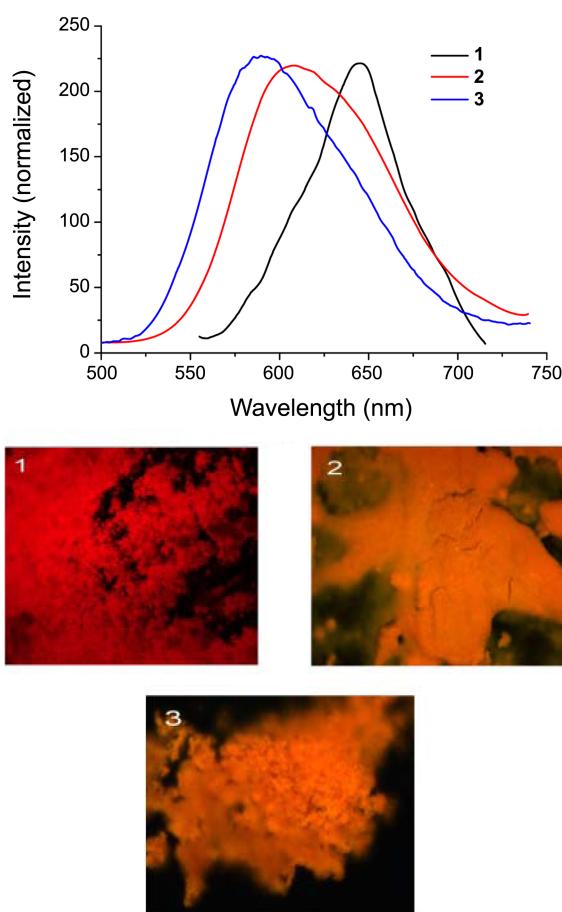


Figure 2. The spectra of solid state fluorescence of **1-3** (up), and the solid state fluorescence pictures of **1-3** (down).

respectively (Table 2). Compounds **2** and **3** have similar structures and electrochemical potentials. The LUMO values of these compounds were all lower than that of BODIPY (-3.05 eV) and the commonly used current electron-transport materials Alq_3 (-3.0 eV).¹⁰ The better electron-accepting features of compounds **1-3** highlight their potential applications as charge-transport materials.

To explore the possibility of using these compounds in OLED devices, thin films were fabricated and the condition of these films were tested (Figure 3). The thin films were fabricated on silicon slices with a $1 \times 1 \text{ cm}^2$ active area. The silicon slices were cleaned with acetone and ethanol, followed by a treatment with 2% (v/v) Hellmanex. As compound **2** has a better solubility than compounds **1** and **3**, the films were first spin-coated using 0.01 g/mL of compound **2** in toluene and dried at 20°C for 10 min in N_2 . For each sample, the rotation speed was set to produce a >60 nm-thick film. After the wet process, the thin films were examined by atomic force microscopy. As shown in Figure 3, the continuous and well-formed thin film of compound **2** insured its application as an emission material or electron transporting material in future OLED studies.

In summary, novel bi-nuclear boron complexes with a pyrene ligand were synthesized and characterized. Significant features, such as strong fluorescence in the solution and

Table 2. Electrochemical Potentials and Energy Levels of **1-3**

Cmpd	HOMO (eV)	LUMO ^a (eV)	LUMO ^b (eV)	E _g (eV) ^a	E _g (eV) ^b
1	-5.59	-3.66	-3.61	1.93	1.98
2	-6.02	-3.60	-3.23	2.42	2.79
3	-6.02	-3.59	-3.25	2.43	2.77

E_g^a : calculated from cyclic voltammetry. E_g^b : the value estimated by using the UV-vis absorption edge in solid state. LUMO^a: the value from cyclic voltammetry. LUMO^b: calculated from the HOMO and E_g^a

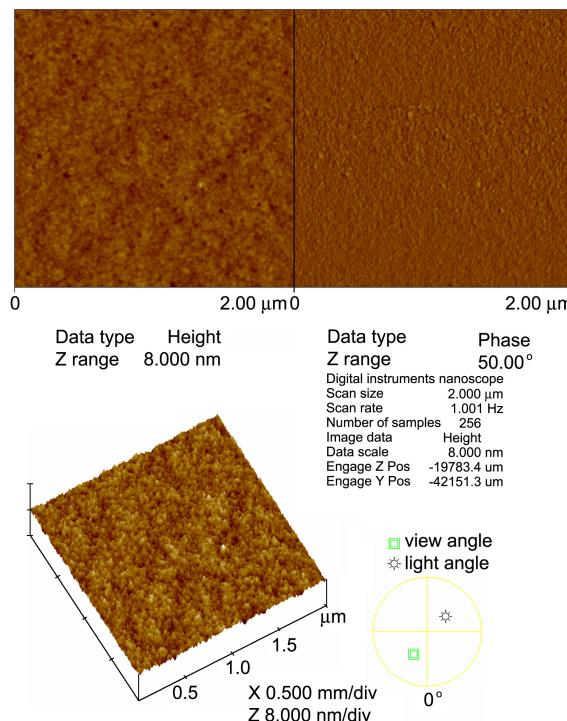


Figure 3. The AFM (Atomic Force Microscope) photo of the thin film of **2** on silicon.

solid states, lower LUMO and higher HOMO levels, were observed in these three boron complexes **1-3**. Thin films of compound **2** were confirmed by atomic force microscopy to be continuous and well-formed, making this compound suitable for the further OLED studies. These novel boron complexes are multifunctional candidates for use in light-emitting or electron transporting applications.

Experimental Section

Electrochemical Properties. CV was carried out at a potential scan rate of 100 mV/s in a 0.1 M solution of TBABF₄ (tetra-n-butylammoniumtetrafluoroborate) in DMSO and anhydrous dichloromethane. All of the electrochemical experiments were performed in a glove-box under an Ar atmosphere at room temperature. A platinum wire and an Ag/AgNO₃ electrode were used as the counter electrode and reference electrode, respectively. The energy level of the Ag/AgNO₃ reference electrode (calibrated by) was 4.76 eV below the vacuum level. HOMO levels were calculated according to the empirical formula $E_{\text{HOMO}} = -([E_{\text{onset}}]^{\text{ox}} +$

4.76 (eV), with the onset oxidation potentials measured by cyclic voltammetry.

Synthesis of compound CB1. To 15 mL dichloromethane solution of 0.216 g of 1, 2-phenylenediamine, a solution of 1 g **P3** in 20 mL dichloromethane was added drop-wise during 30 minutes with stirring. The mixture was then stirred at room temperature for 48 hours, and the solvent was evaporated. After adding the CH₃OH, the powder was filtered and recrystallized by CHCl₃ to obtain orange powder of **CB1**. Yield: 0.39 g (69 %) ¹H NMR (DMSO, 250 MHz) δ 14.52 (s, 2H), 9.43 (s, 1H), 8.50-8.30 (m, 2H), 8.17-7.81 (m, 15H), 7.55 (s, 2H), 7.33 (s, 2H). HRMS (FAB): *m/z* = 579.2077 [M + H]⁺, calc. for C₄₀H₂₅N₂O₂ = 579.2073.

Synthesis of 1. 0.5 mL *N*-Ethylidiisopropylamine and 1 mL BF₃·Et₂O were added to the solution of 0.57 g compound **CB1** (1 mmol) in 15 mL toluene. The mixture was stirred under nitrogen for 2 hours at 40 °C. After the toluene was removed, the residues were purified by silica gel column chromatography using dichloromethane as eluent to afford red compound **1**. Yield: 0.38 g (58 %) ¹H NMR (CDCl₃, 250 MHz) δ 9.04 (s, 1H), 8.57-8.53 (d, 1H), 8.11-7.66 (m, 16H), 7.19-7.16 (m, 4H). HRMS (FAB): *m/z* = 660.1777 [M + H]⁺, calc. for C₄₀H₂₂B₂F₄N₂O₂ = 660.1804.

Synthesis of CB2. Starting from 0.27 g *p*-xylylenediamine and 1 g **P3**, **CB2** was synthesized by the same procedure as that for **CB1** described above. Yield: 0.71 g (60 %) ¹H NMR (CDCl₃, 250 MHz) δ 8.86 (s, 2H), 8.50 (s, 1H), 8.04-7.97 (m, 9H), 7.68 (s, 2H), 7.46 (s, 4H), 6.84 (s, 4H), 4.99 (s, 4H). HRMS (FAB): *m/z* = 593.2233 [M + H]⁺, calc. for C₄₂H₂₉N₂O₂ = 593.2229.

Synthesis of 2. **2** was prepared from **CB2** (0.6 g) and 0.5 mL *N*-ethylidiisopropylamine and 1 mL BF₃·Et₂O by a procedure similar to that described for the preparation of compound **1**. The powder was filtered and recrystallized by CH₂Cl₂ to obtain orange powder of **2**. Yield: 0.4 g (60 %) ¹H NMR (DMSO, 250 MHz) δ 9.47 (s, 2H), 8.50-8.42 (m, 4H), 8.26-7.94 (m, 14H), 7.58 (s, 4H), 5.11 (s, 4H). HRMS (FAB): *m/z* = 688.2131 [M + H]⁺, calc. for C₄₂H₂₇B₂F₄N₂O₂ = 688.2114.

Synthesis of CB3. Starting from 0.27 g *m*-xylylenediamine and 1 g **P3**, **CB3** was synthesized by the same procedure as that for **CB1** described above. Yield: 0.77 g (65 %) ¹H NMR (CDCl₃, 250 MHz) δ 14.50 (s, 2H), 8.84 (s, 2H), 8.48-8.44 (d, 2H), 8.04-7.76 (m, 16H), 7.43-7.36 (m, 4H), 4.99 (s, 4H). HRMS (FAB): *m/z* = 593.2226 [M + H]⁺, calc. for C₄₂H₂₉N₂O₂ = 593.2229.

Synthesis of 3. **3** was prepared from **CB3** (0.6 g) and 0.5 mL *N*-ethylidiisopropylamine and 1 mL BF₃·Et₂O by a procedure similar to that described for the preparation of compound **1**. The powder was filtered and recrystallized by CH₂Cl₂ to obtain orange powder of **3**. Yield: 0.4 g (60 %) ¹H NMR (DMSO, 250 MHz) δ 9.52 (s, 2H), 9.37-7.84 (m, 16H), 7.64-7.53 (m, 4H), 5.27 (s, 4H). HRMS (FAB): *m/z* = 688.2119 [M + H]⁺, calc. for C₄₂H₂₇B₂F₄N₂O₂ = 688.2131.

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