

Novel binaphthyl-containing bi-nuclear boron complex with low concentration quenching effect for efficient organic light-emitting diodes†

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OLEDs employing CMB1, a novel binaphthyl-containing bi-nuclear boron complex, as the emitter exhibited bright yellow emission with a luminous efficiency of 2.1 cd A⁻¹.

Significant progress has been made in organic light-emitting diodes (OLEDs) for display and solid-state lighting applications over the past few decades.^{1,2} The notable advantages of the well-designed organic molecules, such as well-defined molecular structures, facile synthesis, purification and modification, and specific structure–property correlations, are the major reasons that have ensured their widespread applications in optoelectronic devices.³

Some organic fluorine–boron complexes, as the analogues of BODIPY (dipyrrro-boradiazaindacenes), have been reported to achieve high solid state emission intensity or be promising electron transporting materials in OLEDs.⁴ However, for BODIPY and its derivatives,⁵ which are the best-known fluorophores, the strong intermolecular interactions and typical small Stokes shifts lead to luminescence quenching in the solid state and a decrease in the device performance that limit their applications in OLEDs. Consequently, there has been increasing interest in the development of novel boron complexes with a well-designed structure to overcome the weakness of BODIPY as well as control the optical properties, improve their electron-accepting capability and apply them successfully with high efficiency.

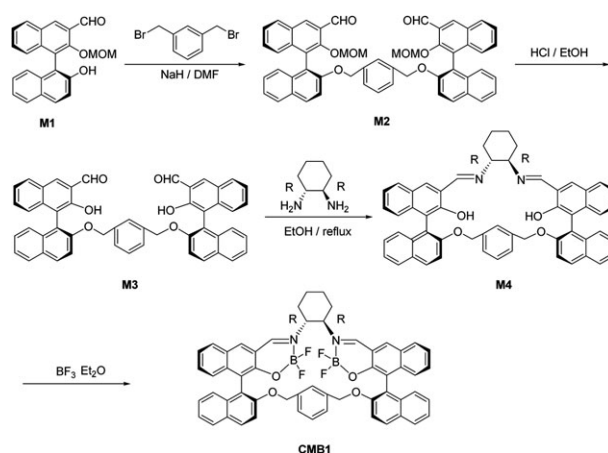
In the design of the target molecule, bi-nuclear boron complex centers were introduced to ensure strong fluorescence intensity and electron-transporting property. (1*R*,2*R*)-(–)-1,2-cyclohexanediamine and 1,3-bis(bromomethyl)benzene were introduced as linkers and non-planar binaphthyl units were introduced to the fluorophore to prevent intermolecular interactions in the solid state. Although the large dihedral angle and twisted conformation of the binaphthyl unit yield a

stable amorphous phase that can increase the luminescence intensity,⁶ there are no reports of the connection of two binaphthyl units to form fixed twisted-planes, reduce solid state quenching and achieve stronger fluorescence.

This paper reports a highly efficient yellow emitting material (CMB1) based on a novel bi-nuclear boron complex using the binaphthyl unit as the fluorophore and OLEDs based on CMB1. CMB1 showed low concentration quenching with a photoluminescence quantum yield (PLQY) of 10% in the solid state as well as good electron transporting ability. The OLED employing the material as an emitter showed bright yellow emission with a luminous efficiency of 2.1 cd A⁻¹.

The synthesis of CMB1 (Scheme 1) began from M1, which was synthesized according to the reported procedure.⁷ The reaction of M1 with *m*-xylylene dibromide in DMF afforded MOM-protected binol dimer M2 in 82% yield. M3 was synthesized by the further deprotection of M2 in ethanol with a few drops of concentrated hydrochloric acid. In absolute ethanol, the condensation of M3 with (1*R*,2*R*)-(–)-1,2-cyclohexanediamine gave M4 in 82% yield. CMB1 was synthesized in high yield (70%) by reacting M4 with BF₃ in toluene at 40 °C. The detailed procedures and characterization of the new compounds are explained in the supporting information.

The absorption and fluorescence properties of CMB1 were tested in both the solution and solid state. Fig. S11 shows the absorption spectra of CMB1 in solution (supporting information). Based on the absorption edges of CMB1 in the solid state, the corresponding optical energy gap (E_g) was calculated to be 2.49 eV. (Table 1) As shown in Fig. 1, compound CMB1 exhibited an emission band centered at



Scheme 1 The synthetic route of the compound CMB1.

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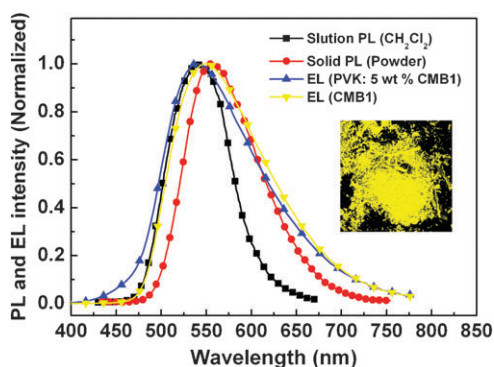


Fig. 1 Fluorescent spectra of compound **CMB1** in solution (black, 20 μM in dichloromethane) and in the solid state (red, powder) and electroluminescent spectra of devices with PVK: 5 wt% **CMB1** (blue) and neat **CMB1** (yellow) as emitting layers. Inset: the solid state fluorescence of the powder of **CMB1**.

540 nm in dichloromethane when excited at 430 nm, and the **CMB1** powder showed very strong yellow emission at 556 nm when excited at 400 nm. (Fig. 1, Inset picture).

Compared with the emission spectrum of the dilute solution, the powder spectrum of **CMB1** was red-shifted and a little broader than that of solution due to the non-radiative decay caused by intermolecular interaction and inhomogeneous broadening effects. But it should be pointed out that the bathochromic-shift and the shapes of the fluorescent peaks in solution and the solid state changed very little (fwhm = 91 nm in dichloromethane; fwhm = 93 nm in powder). This phenomenon indicated that the highly twisted structure and the steric hindrance of the cyclohexane and binaphthyl moiety successfully decreased the intermolecular interactions in the film compared with our previous work.^{4c} Reduction of the intermolecular interaction has been further confirmed by the PLQY of the material shown in Fig. S12 (supporting information). The neat **CMB1** film showed a PLQY of $\sim 10\%$, almost the same as the dilute solid solution of **CMB1** in poly(*N*-vinylcarbazole) (PVK), indicating that concentration quenching is negligible.

Table 1 summarizes the electrochemical potentials and energy levels of **CMB1**. The HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) levels were calculated using empirical equations with the onset oxidation and reduction potentials measured by cyclic voltammetry.⁸ During the anodic scan, **CMB1** exhibited reversible oxidation processes, indicating suitable electrochemical stability for p-doping processes. According to the $E_{\text{ox}}^{\text{onset}}$ and $E_{\text{red}}^{\text{onset}}$ values, the calculated HOMO and LUMO of **CMB1** were -3.53 eV and -6.08 eV, respectively.

Table 1 Electrochemical potentials and energy levels of **CMB1**

Cmpd	Condition	HOMO/eV	LUMO/eV	E_g /eV
CMB1	Vcv	-6.08	-3.53	2.55
	Vca	-5.03	-3.41	1.62
	Vcg	-6.08	-3.59	2.49

Vcv: calculated from cyclic voltammetry. Vca: calculated from the quantum chemical calculation. Vcg: HOMO value was calculated by CV and the LUMO value was determined from the HOMO level and the optical band gap, which was calculated from the onset value of the optical absorption spectra in the solid state.

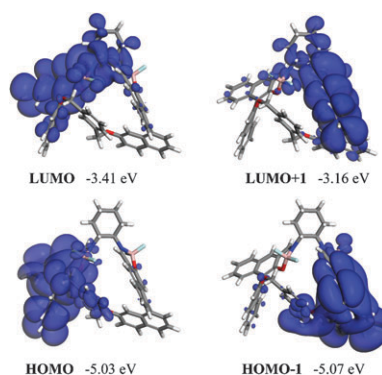


Fig. 2 The calculated HOMO and LUMO levels of **CMB1**.

The band gap calculated from the electrochemical measurement was 2.55 eV, which is slightly higher than the one (2.49 eV) obtained from the absorption spectrum and calculation data (1.62 eV).

Ab initio calculations were performed based on density-functional theory using VASP code to obtain more details on the electronic structure.⁹ Fig. 2 shows the charge distribution of HOMO-1 and LUMO+1 of **CMB1**. The HOMO and HOMO-1 were distributed mostly over the paired naphthalene molecules on each wing of **CMB1**. Due to the symmetrical structure of **CMB1**, the HOMO and HOMO-1 were almost degenerate. Similarly, the LUMO and LUMO+1 were related symmetrically because they are localized at the naphthalene group close to the cyclohexane group.

Fig. 3 shows the structures of the OLEDs as well as the energy levels of the constituent materials. Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, 40 nm) was used as the hole injection layer. 4,4',4''-Tris(carbazol-9-yl)triphenylamine (TCTA, few nm) was used as both the hole transporting and electron blocking layer. Bis-4,6-(3,5-di-3-pyridylphenyl)-2-methylpyrimidine (B3PYMPM, 50 nm) was employed as the electron transporting layer. A 40 nm thick neat **CMB1** film (device I) and **CMB1** doped in PVK films (devices II-V) were used as the light emitting layer (EML) in the OLEDs. The doping concentrations in PVK were varied: 20 (device II), 15 (device III), 10 (device IV) and 5 wt% (device V). A device without a TCTA layer (device VI) was also fabricated using neat **CMB1** as the emitter to examine the electron transport of **CMB1** by eliminating the electron blocking layer.

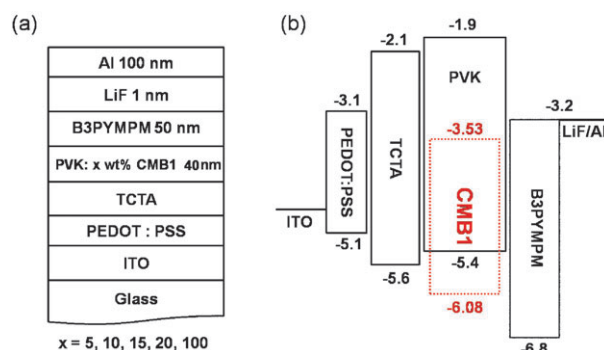


Fig. 3 (a) The structures of OLED devices and (b) the energy diagram of the devices.

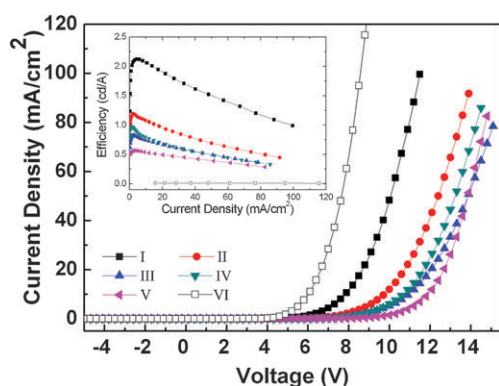


Fig. 4 Current density–voltage characteristics of devices I, II, III, IV, V and VI. Inset: Current density–efficiency curves of devices. Voltage–luminescent curves are shown in Fig. S15 (supporting information).

Fig. 4 presents the current density–voltage–luminescence characteristics of the devices. A higher current was obtained with increasing **CMB1** doping concentration in PVK, resulting in the highest current in the neat **CMB1** OLED. This behavior can be understood by the electron transporting properties of **CMB1**. The current level with a low **CMB1** concentration (5 wt% in PVK) was quite low due to the low mobility of holes and negligible mobility of electrons in PVK. Increasing the **CMB1** concentration in PVK allowed the electrons to be transported *via* **CMB1** through hopping to recombine with the holes injected from TCTA, resulting in an increase in efficiency (inset of Fig. 4) with increasing **CMB1** concentration. This suggests that the **CMB1** molecules contribute to electron transport in the devices, which is supported by the largest current in the neat **CMB1** OLED. Although a higher current was obtained in the neat **CMB1** OLED without the TCTA electron blocking layer (device VI), the device showed a very low efficiency of 0.014 cd A^{-1} due to the electron dominant current. This provides further evidence of the excellent electron transporting ability of **CMB1**. The zero field electron mobility was estimated using an electron only device and it turns out to be $\sim 10^{-7} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The mobility is in a similar range to the well known electron transporting materials being used in OLEDs. (Fig. S16, supporting information).

Another advantage of **CMB1** in terms of OLED fabrication originates from the low concentration quenching of the material in the neat films, allowing the fabrication of OLEDs without the development of a host. The luminous efficiency was the highest in the neat **CMB1** OLED (2.1 cd A^{-1} at 100 cd m^{-2}), as shown in the inset in Fig. 4. Considering the singlet/triplet ratio of excitons, the outcoupling efficiency of the light emitted in OLEDs and the PLQY of 10% for **CMB1**, the external quantum efficiency of 0.74% corresponding to a luminous efficiency of 2.1 cd A^{-1} reflects the very good charge balance between electrons and holes in the devices.¹⁰ The low concentration quenching resulted in only a little shift in the maximum EL wavelength from 540 in the 5% doped OLED to 548 nm in the neat **CMB1** OLED shown in Fig. 1.

In conclusion, a novel bi-nuclear boron complex **CMB1**, containing the binaphthyl moiety and (1*R*,2*R*)-(–)-1,2-cyclohexanediamine, was developed to reduce solid state quenching. A combination of the electron transporting ability and low

quenching concentration of the **CMB1** provides OLEDs with unique opportunities due to the rarity of material systems that possess both properties simultaneously. Even though the efficiency of the device is not the highest ever reported,¹¹ further improvement in PLQY is expected to result in high efficiency OLEDs, which is in progress now.

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