Supporting Information for

Novel Binaphthyl-Containing Bi-Nuclear Boron Complex with Low Concentration Quenching Effect for Efficient Organic Light-Emitting Diodes

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Experimental Section

General Information: All reactants and solvents, unless otherwise stated, were purchased from commercial sources and used as received. Flash chromatography was carried out on silica gel (230-400 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded using 250 MHz. Chemical shifts were expressed in ppm and coupling constants (J) in Hz. Mass spectra were obtained using JEOL JMS-700 Mstation spectrometers. The thermal analyses were carried out on TGA Shimadzu DTG-60H, DSC-N650 a nalyzer under a nitrogen atmosphere at heating rate of 10 °C min^{-1}. The absorption and PL spect ra in solutions were measured by using a Scinco S-3100 UV-vis spectrometer and Shimadzu RF-5301 PC fluorescence spectrophotometer, respectively. The absorption and PL spectra in solid stat e were measured by using a VARIAN 5000 UV-vis-NIR spectrophotometer and Perkin Elmer LS 55 Fluorescence spectrometer, respectively.

Electrochemical Properties: CV was carried out at a potential scan rate of 100 mV s^{-1} in a 0.1 M solution of TBABF4 (tetra-n-butylammoniumtetrafluroroborate) in anhydrous dichloromethane. All of the electrochemical experiments were performed in a glove-box under an Ar atmosphere at room temperature. The oxidation and reduction cycles of **CMB1** was measured in dichloromethane solution using the Ferrocine/Ferrocine^{+} redox system as the reference and using tetrabutylammonium hexafluorophosphate as the electrolyte. A platinum wire and an Ag/AgNO$_3$ electrode were used as the counter electrode and reference electrode, respectively. HOMO (highestest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) levels were calculated according to the empirical equations: E_{HOMO} (eV) = $-e(E_{\mathrm{ox}}$ (V vs. SCE) + 4.74 V) and E_{LUMO} (eV) = $-e(E_{\mathrm{red}}$ (V vs. SCE) + 4.74 V), with the onset oxidation and reduction potentials measured by cyclic voltammetry.

Ab-initio Calculations: Calculations on the ground and excited electronic states of the B-F complex was carried out using a first-principles calculation based on density-functional theory with the VASP code.[1] Projector-augmented wave (PAW)[2] potential was adopted to account for the ion-electron interactions, and the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE)[3] functional to describe the exchange correlations between electrons. The energy cut-off for the planewave basis was set to 500 eV and only the Gamma point was employed for the Brillouin zone sampling. The **CMB1** molecule was placed in a relatively large cell of 25 × 25 × 25 Å^3 and the geometry was relaxed until the atomic force on each atom was reduced to within 0.02 eV/Å.

Fabrication of OLED Devices and Testing: The OLED devices were fabricated on patterned indium tin oxide (ITO) glasses. ITO glasses were cleaned using acetone and isopropanol followed by UV-O$_3$ treatment. Then poly(3, 4-ethylenedioxythiophene) (PEDOT): poly(styrenesulfonate) (PSS), the hole injection layer, was spin-coated and heated on a hotplate at 200°C for 5 minutes forming 40 nm thick films. Subsequently solution of 4, 4',4" tris(carbazol-9-yl)-triphenylamine (TCTA) 0.5 wt% in toluene was spincoated and dried at 180°C for 30 minutes.[4] For light emitting layers, either pure CMB1 or four different composition of CMB1 dispersed in poly-(vinylcarbazole) (PVK) films were used. To form neat

CMB1 film, 4 mg of CMB1 was dissolved in 1 ml of toluene, spin-casted, and dried at 150°C for 30 minutes. CMB1 contents in the PVK films were 5, 10, 15, and 20% in weight. Films were spin-coated using chlorobenzene as the solvent, and dried at 150°C for 30 min in N_2. For each solution, rotation speed was controlled to have 40 nm-thick films. After the wet process, devices were moved into a vacuum chamber to deposit hole blocking layer and cathode: 50 nm of bis-4,6-(3,5-di-3-pyridylphenyl)-2-methylpyrimidine (B3PYMPM), 1 nm lithium fluoride (LiF) layer and 100 nm aluminum layer were thermally evaporated under the pressure of 1×10^{-7}torr. Finally devices were encapsulated in the N_2 environment. Current density-voltage-luminescence characteristics of OLEDs were measured using Keithley 2400 source meter and SpectraColorimeter PR650.

Measurement of photoluminescent quantum yield: The experimental procedure and apparatus for the measurement of PLQY closely follow the ones described by Jeong*et al.*[5] The schematic experimental setup comprises a8 inch integrating sphere, aHe:Cd CW laser with 325 and 442 nm, and a monochromator with a photomultiplier tube. Samples are made using either spincastingordropcastingmethods on quartz substrates

The measurement of electron mobility

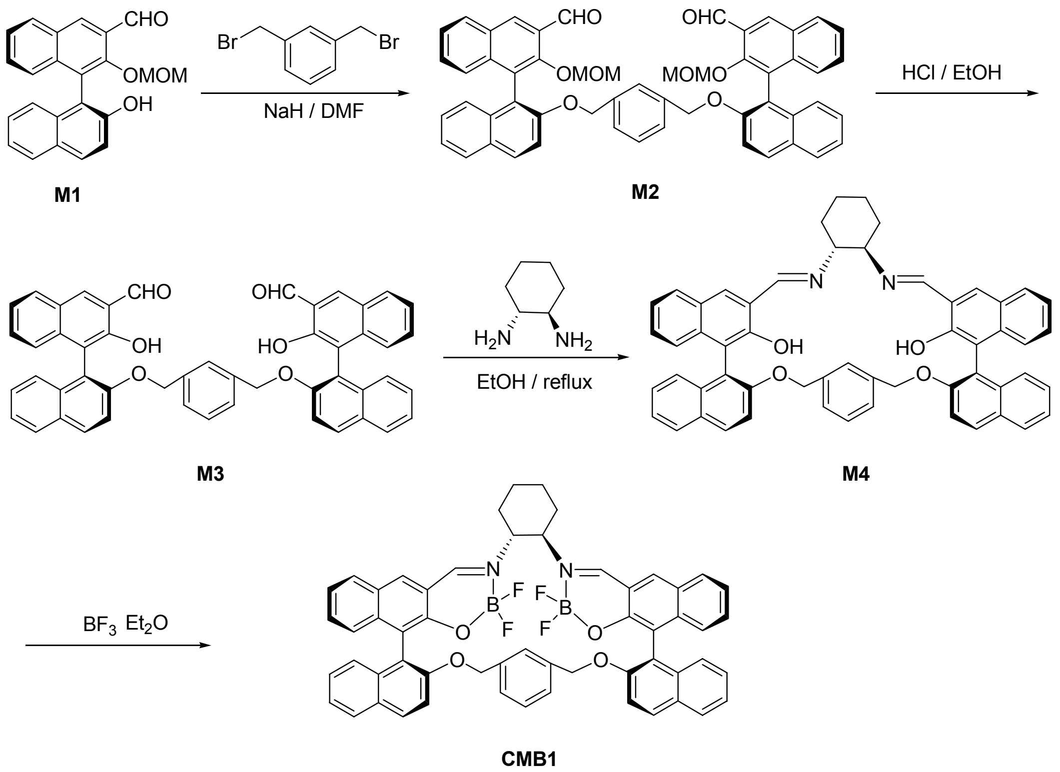
The electron mobility of CMB1 was estimated using an electron only device consisting of Al/40 nm thick CMB1 layer/25 wt% Rb_2CO_3 doped B3PYMPM (40 nm)/Al as shown in the inset of Figure S16. The 25 wt% Rb_2CO_3 doped B3PYMPM was used to improve the electron injection from the Al electrode and to reduce the series resistance coming from the layer. The doped layer has the 100 ~1000 times higher conductivity than the undoped layer so that its resistance for the charge transport in the device can be neglected.

The current density–voltage curve is displayed in Figure S16. The electron mobility was extracted from the space charge limited current region in the J-V curve using the Poole-Frankel type field dependent mobility with shallow traps[6].

$$J(V) = \frac{9}{8}\varepsilon_0\varepsilon_r\mu_0 \exp\left(0.89\gamma\sqrt{V/L}\right)\frac{V^2}{L^3}, \tag{1}$$

where dielectric constant of the material is assumed as $\varepsilon_r = 3$, μ_0 is the zero field mobility, γ is the field enhancement factor, and L is the thickness of the film.

The SCLC fit [$\mu_0 = 2\times10^{-7}$ $\mathrm{cm^2/V\cdot sec}$, $\gamma = 0.003$ $(\mathrm{cm/V})^{0.5}$] and measurements nicely agree at high voltage >2 V, where the space charges are built up. The γ value is comparable with the reported values for different charge transporting materials confirming pertinent of the analysis. The zero field mobility of $\sim10^{-7}$ is a similar value with that of BAlq[6] and Alq_3[7], generally used electron transporting materials in OLEDs.



Scheme S1. The synthesis route of the compound **CMB1**

Synthesis of **M2**: **M1** was synthesized by the reported procedure.[1] To an ice-cooled DMF (50 mL) solution of Mono mom protected binol aldehyde **M1** (4.0 g, 11.2 mmol), sodium hydride (0.346 g, 14.56 mmol) was added and stirred for 1 hour. M-xylelene dibromide (1.46 g, 5.6 mmol) was then added slowly to the above mixture. After stirring overnight, the reaction mixture was quenched and extracted with ethyl acetate several times. The organic layer was dried and evaporated, and the residue was purified by silica gel column chromatography using chloroform/hexane (1: 3, v/v) as eluent to obtain a pale yellow solid of **M2**.Yield: 5.6 g (81.7 %) 1H NMR ($CDCl_3$, 250 MHz) δ (ppm): 10.58 (s, 2H), 8.55 (s, 2H), 7.99-7.84 (m, 6H), 7.38-7.14 (m, 14H), 6.88 (t, 1H), 6.75 (d, 2H), 6.56 (s, 1H), 4.86 (q, 4H), 4.65 (dd, 4H), 2.90 (s, 6H). 13C NMR ($CDCl_3$, 62.5 MHz) δ (ppm): 191.27, 154.09, 154.00, 137.08, 137.01, 133.84, 131.00, 130.40, 130.21, 129.25, 129.13, 128.31, 128.18, 127.11, 127.02, 126.09, 125.92, 125.28, 125.12, 124.16, 118.86, 114.98, 100.27, 70.66, 57.19.

Synthesis of **M3**: To the MOM-protected binol dimer **M2** (1.0 g, 1.22 mmol) in 25 mL ethanol, a few drops of concentrated hydrochloric acid was added and the mixture was refluxed for 30 min. The solvent was evaporated and recrystallized with ethanol to afford the desired compound **M3**. Yield: 0.88 g (98.6 %). 1H NMR ($CDCl_3$, 250 MHz) δ (ppm): 10.45 (bs, 2H), 10.09 (s, 2H), 8.20 (s, 2H), 7.94-7.85 (m, 6H), 7.35-7.15 (m, 14H), 6.85 (t, 1H), 6.76 (d, 2H), 6.56 (s, 1H), 4.92 (s, 4H). 13C NMR ($CDCl_3$, 62.5 MHz) δ (ppm): 196.91, 154.15, 153.47, 137.90, 137.86, 137.20, 133.65, 130.30, 130.05, 129.78, 129.50, 128.24, 127.51, 128.76, 128.00, 125.41, 124.94, 124.25, 124.02, 122.03, 118.44, 115.75, 71.04.

Synthesis of **M4**: The binol dialdehyde M3 (500 mg, 0.68 mmol) and (1R, 2R)-(-)-1,2-cyclohexanediamine (78 mg, 0.68 mmol) were dissolved in absolute ethanol and heated under reflux for 4 hours. After cooled to room temperature, the precipitate formed was separated and washed with ethanol (ice cold) several times to afford the desired compound M4. Yield: 0.45 g (81.3 %). 1H NMR (CDCl3, 250 MHz) δ (ppm): 12.94 (s, 2H), 8.50 (s, 2H), 8.00 (d, 2H), 7.90 (d, 2H), 7.70-7.52 (m, 4H), 7.48 (d, 2H), 7.40-7.14 (m, 10H), 6.97 (d, 2H), 6.55 (t, 1H), 6.38 (d, 2H), 5.24 (s, 1H), 4.48 (s, 4H), 3.29 (d, 2H), 1.80-1.43 (m, 8H). 13C NMR (CDCl3, 62.5 MHz) δ (ppm): 165.46, 154.66, 154.44, 136.45, 135.47, 133.89, 133.32, 130.20, 129.68, 128.53, 128.24, 128.04, 127.33, 126.60, 125.77, 125.50, 124.78, 124.27, 123.04, 120.45, 118.08, 116.86, 72.82, 33.07, 24.37.

Synthesis of **CMB1**: 0.5 ml N-Ethyldiisopropylamine and 1 ml $BF_3\cdot Et_2O$ were added to the solution of 0.40 g compound **M4** (0.5 mmol) in 15 ml tolune. The mixture was stirred under nitrogen for 1 hour at 40 °C. After the tolune was removed, the residues were purified by silica gel column chromatography using dichloromethane as eluent to afford compound **CMB1**. Yield: 0.32 g (70 %). 1H NMR ($CDCl_3$, 250 MHz) δ (ppm): 8.66 (s, 2H), 8.01-7.98 (m, 2H), 7.89-7.86 (m 2H), 7.70-7.67 (m, 2H), 7.47-7.35 (m, 2H), 7.35-7.26 (m, 2H), 7.13-6.73(m, 9H), 6.76-6.72 (m, 2H), 6.72-6.46 (m, H), 6.44-6.41 (d, 2H), 4.99 (s, H), 4.39-4.34 (d, 4H), 2.23 (m, 5H), 1.96 (m, 2H),1.55 (m, 5H). 13C NMR ($CDCl_3$, 62.5 MHz) δ (ppm): 167.78, 154.30, 138.93, 136.38, 135.42, 133.62, 130.00, 129.00, 127.83, 127.49, 126.66, 126.47, 125.79, 125.48, 125.29, 124.24, 123.90, 120.67, 120.05, 117.90, 116.92, 72.74, 26.12, 24.52. FAB MS m/z = 904.3263 $[M + H]^+$, calc. for $C_{56}H_{42}O_4N_2F_4B_4$= 904.3285.

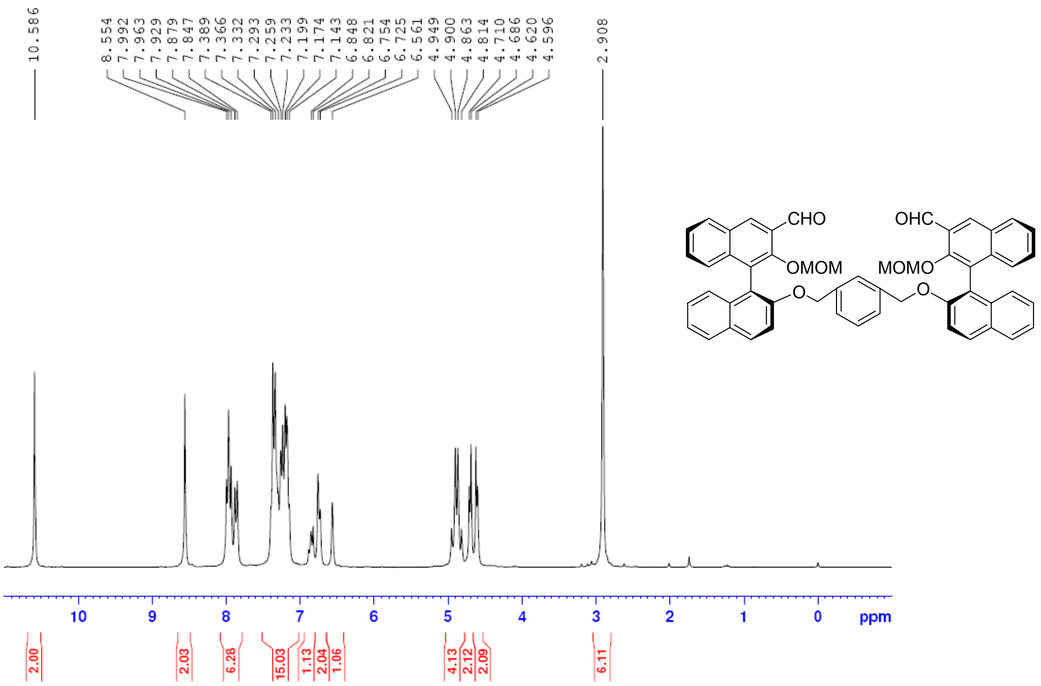


Figure S1. ^{1}H NMR ($CDCl_3$, 250 MHz) spectra of compound **M2**.

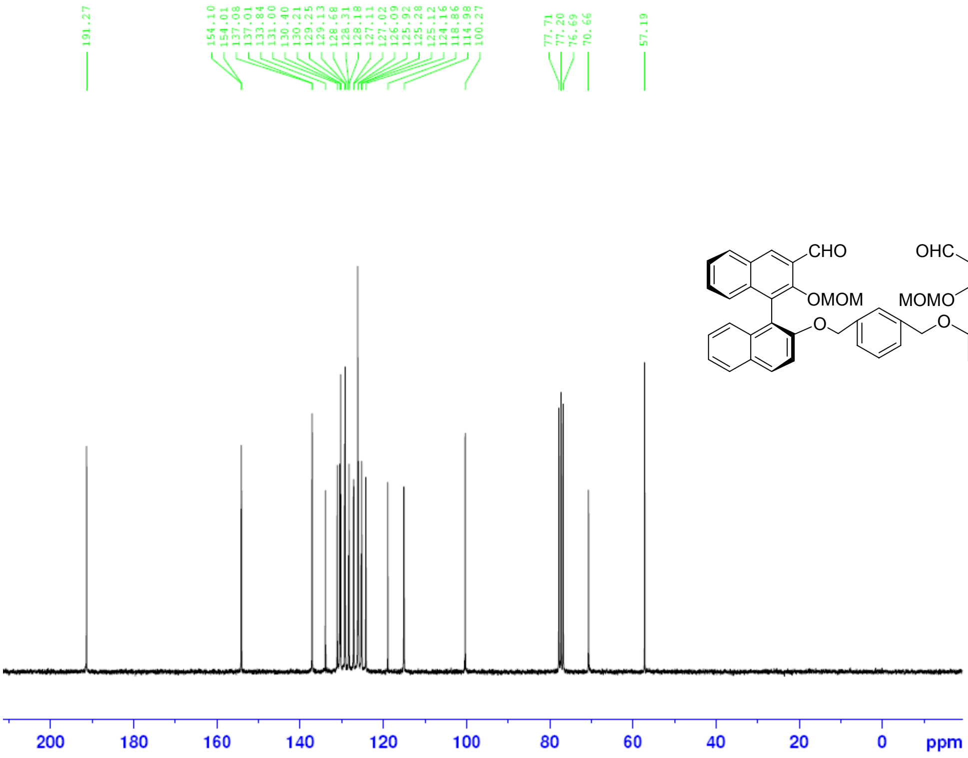


Figure S2. ^{13}C NMR ($CDCl_3$, 62.5 MHz) spectrum of compound **M2**.

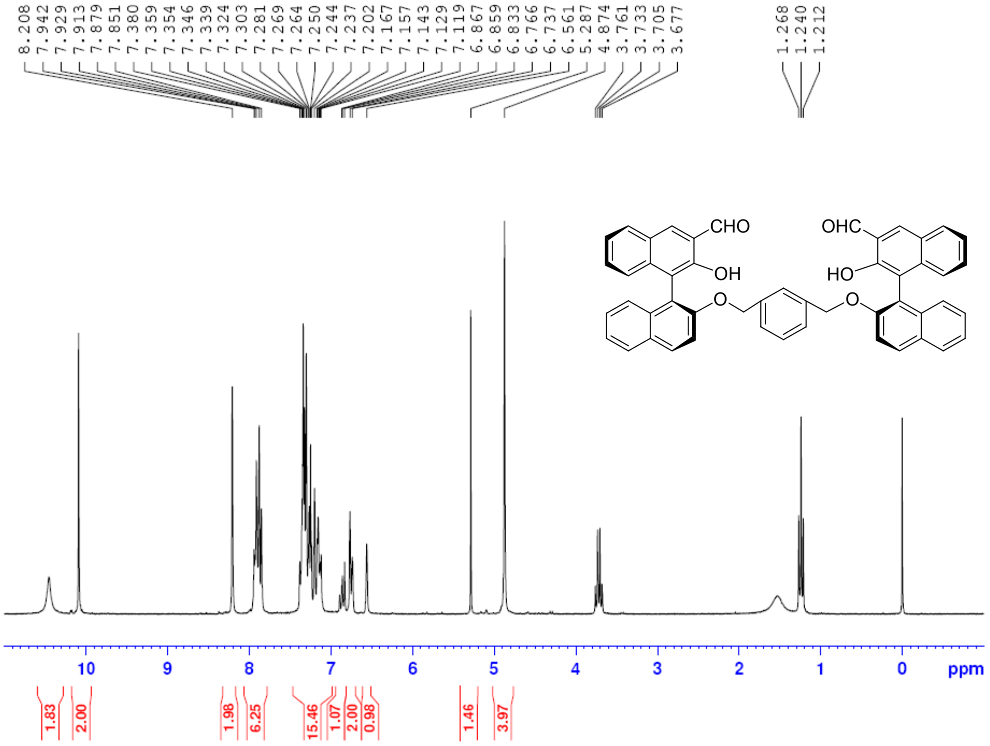


Figure S3. ^{1}H NMR ($CDCl_3$, 250 MHz) spectra of compound **M3**.

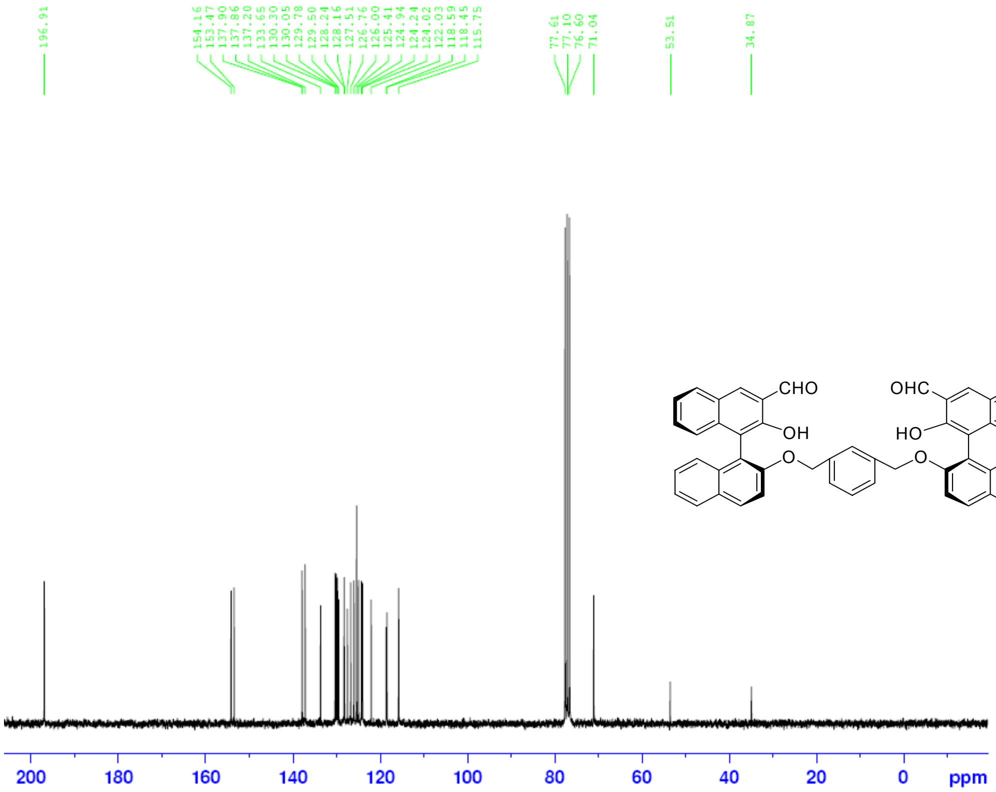


Figure S4. ^{13}C NMR ($CDCl_3$, 62.5 MHz) spectrum of compound **M3**.

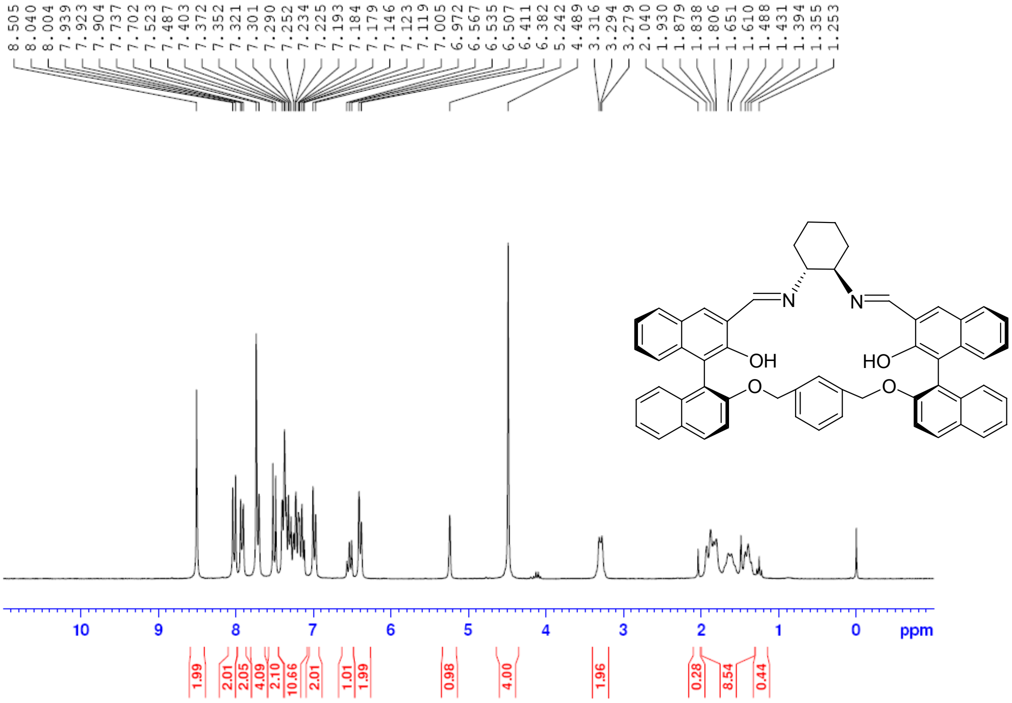


Figure S5. ^{1}H NMR ($CDCl_3$, 250 MHz) spectra of compound **M4**.

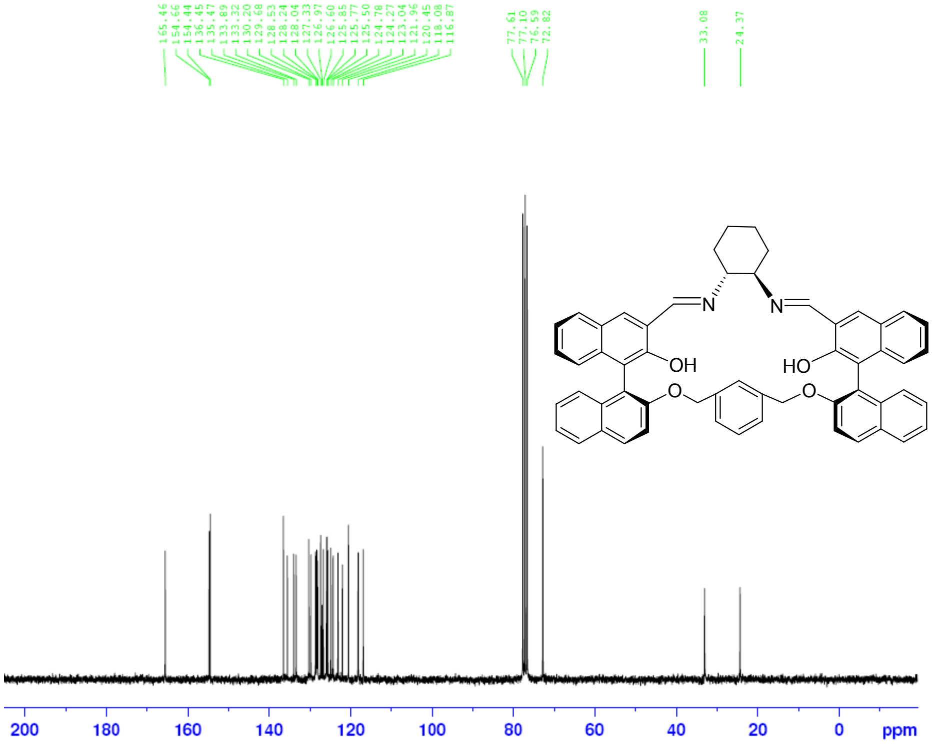


Figure S6. ^{13}C NMR ($CDCl_3$, 62.5 MHz) spectrum of compound **M4**.

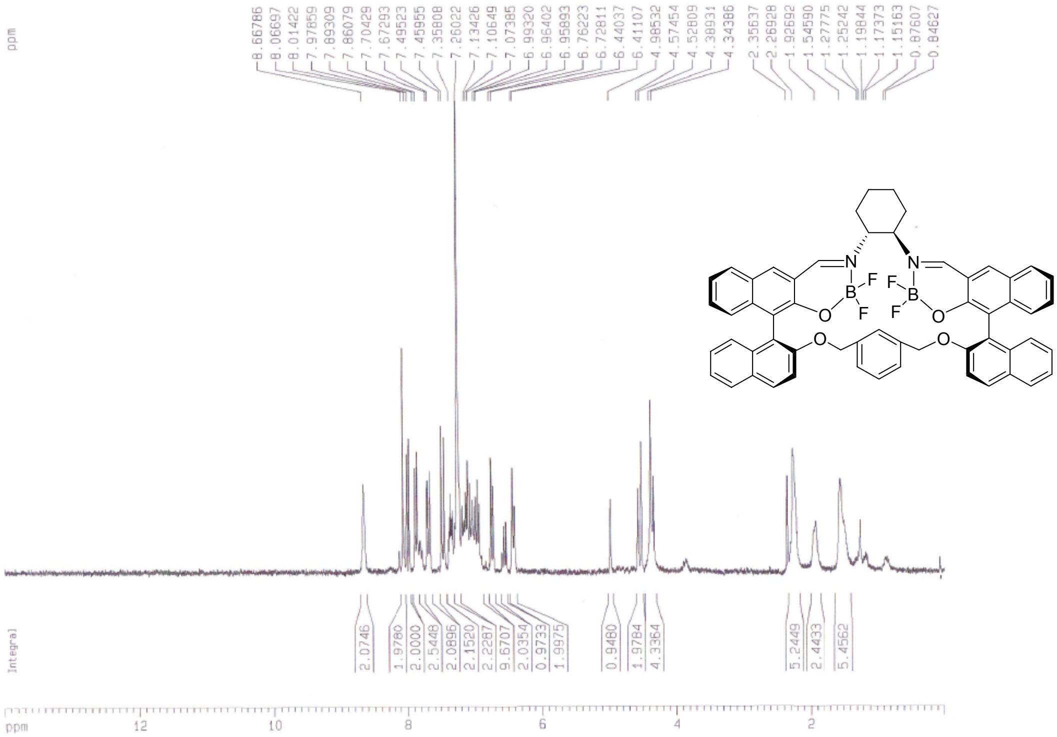


Figure S7. ^{1}H NMR (CDCl$_3$, 250 MHz) spectra of compound **CMB1**.

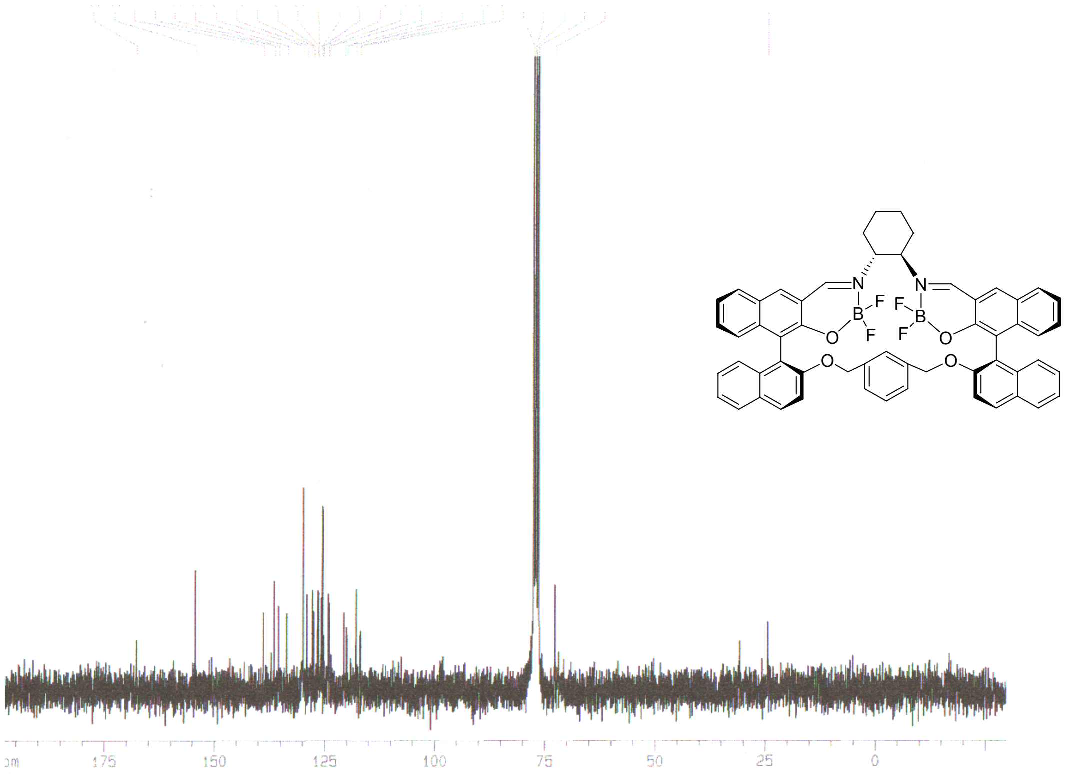


Figure S8. ^{13}C NMR (CDCl$_3$, 62.5 MHz) spectrum of compound **CMB1**.

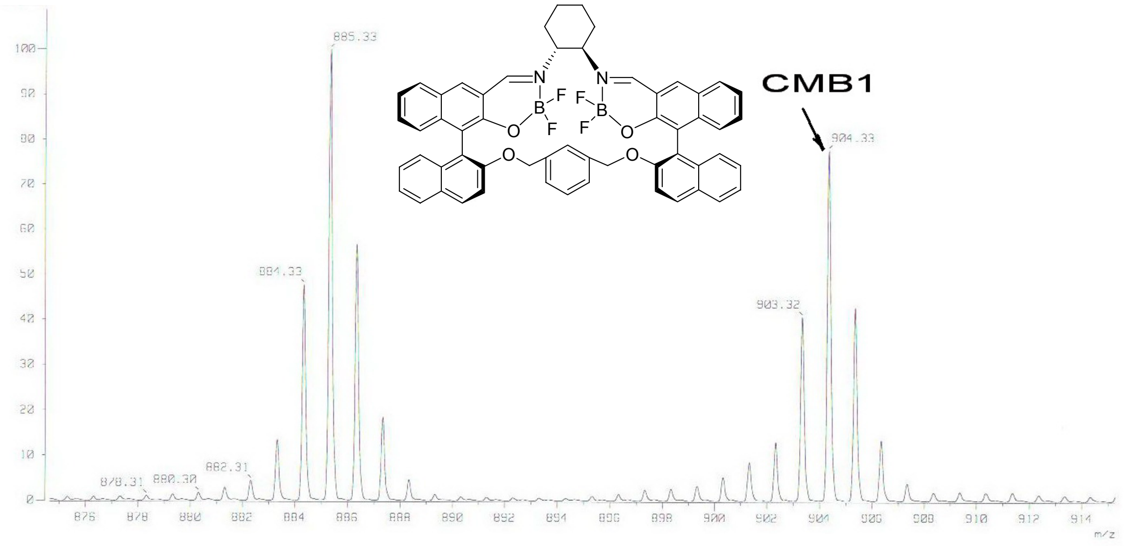


Figure S9. HRMS (FAB) of compound **CMB1.**

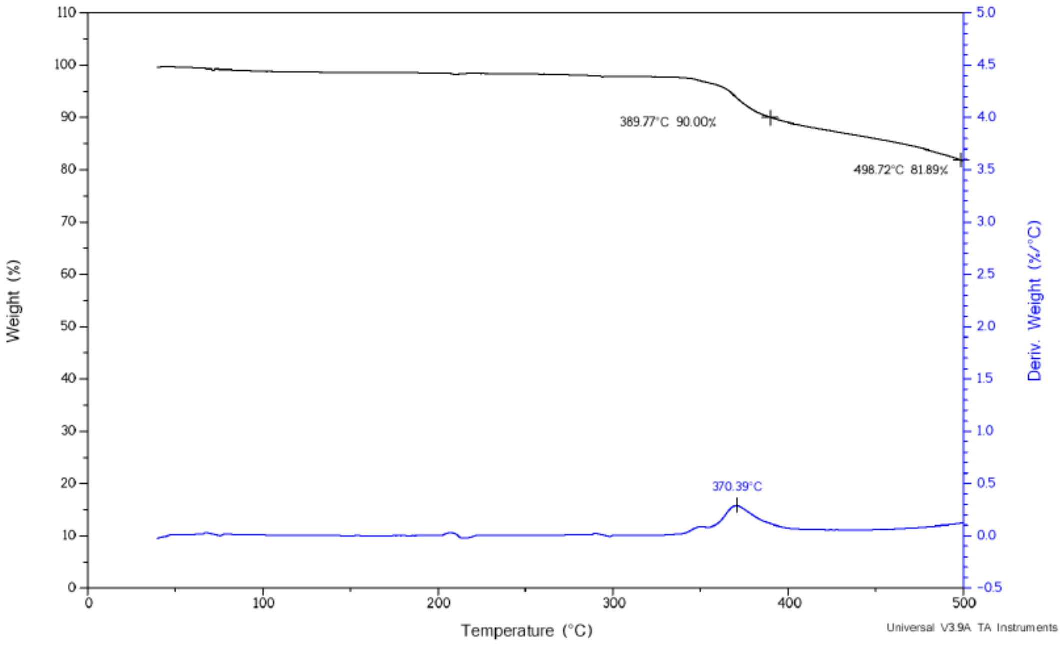


Figure S10. The thermal gravimetric analysis (TGA) test of compound **CMB1**.

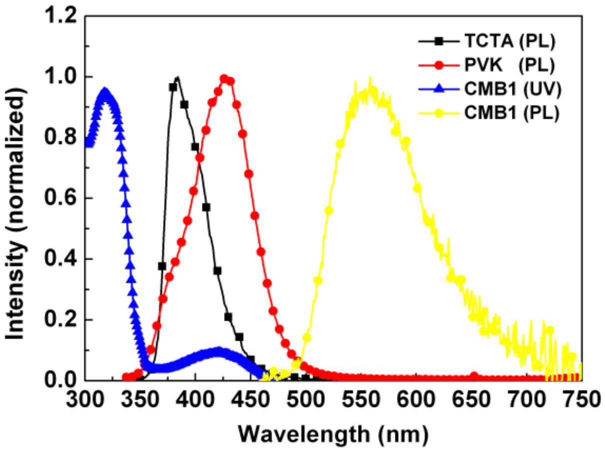


Figure S11. The UV spectrum of compound **CMB1** in solution (20 μM indichloromethane) and the photoluminescence (PL) spectra of **CMB1** (film),TCTA (powder) and PVK (powder) in solid state.

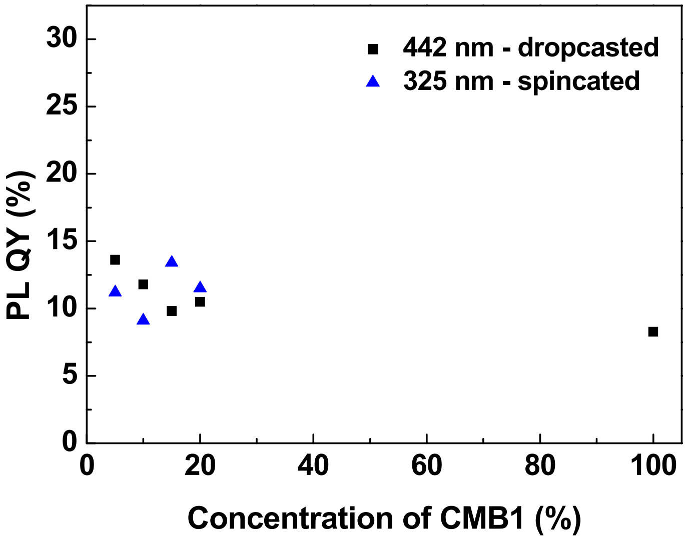


Figure S12. Concentration dependent PLQY of **CMB1** with different excitation wavelengths

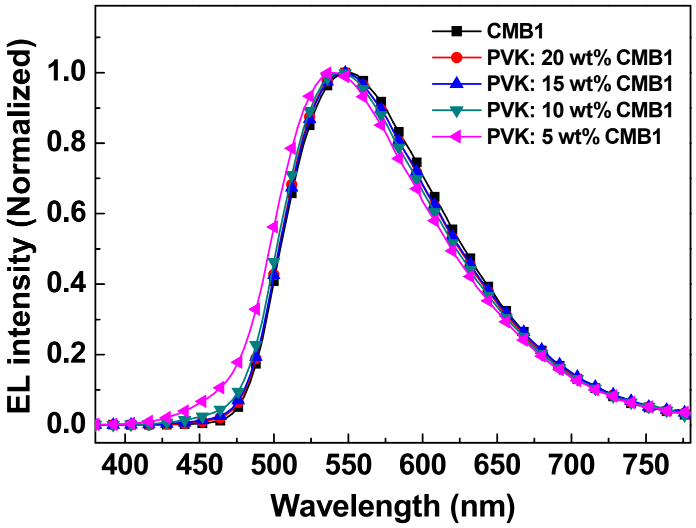


Figure S13. EL spectra of studied devices at brightness of 100 cd/m^2

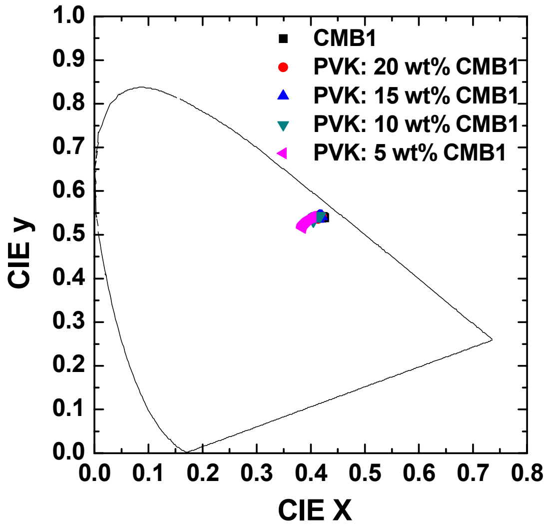


Figure S14. CIE (commission internationale de l'Eclairage) x and y coordinates coordination of the studied devices

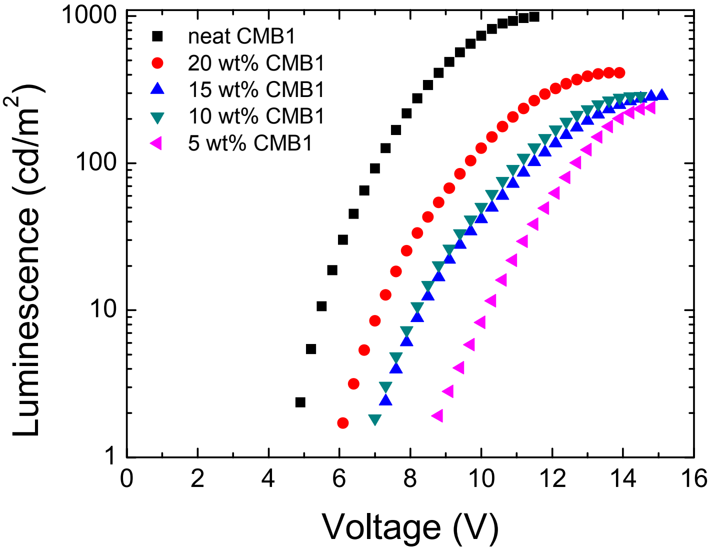


Figure S15. Voltage-luminescence curve of studied devices.

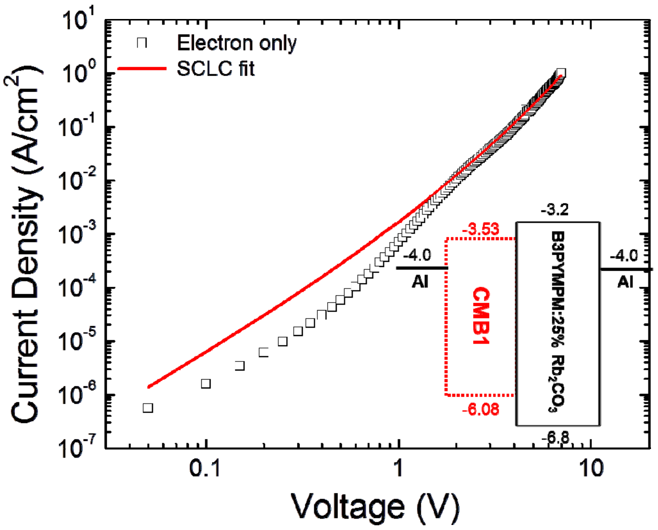


Figure S16. Voltage vs. Current density characteristics of electron only device and its energy diagram. Blank squares are experimental data and red solid line is SCLC fit.

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