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Supporting Information

High triplet energy small molecule based thermally cross-linkable hole-transporting material for solution-processed multilayer blue electrophosphorescent devices

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Table of Contents

General information

Device fabrication

Experimental section

Device characterization

General information:

All chemical and reagents were obtained from commercial suppliers and used without further purification. ^{1}H NMR and ^{13}C HMR spectra were measured on a Bruker ARX300 NMR spectrometer with tetramethylsilane as the internal standard. Elemental analysis was performed on an Elementar Vario EL CHN elemental analyzer. Mass spectrometry was performed with a Thermo Electron Corporation Finnigan LTQ mass spectrometer. Absorption spectra were recorded with a UV-vis spectrophotometer (Agilent 8453) and PL spectra were recorded with a fluorospectrophotometer (Jobin Yvon, FluoroMax-3). The transient photoluminescence characteristics were measured using a transient spectrometer (Edinburg FL920P). TGA was recorded with a Netzsch simultaneous thermal analyzer (STA) system (STA 409PC). Glass-transition temperature was recorded by DSC with a thermal analysis instrument (DSC 2910 modulated calorimeter). The film surface morphology was measured with AFM (Seiko Instruments, SPA-400). Cyclic voltammetry was performed on a Princeton Applied Research potentiostat/galvanostat model 283 voltammetric analyzer. The film surface morphology was measured with AFM (Seiko Instruments, SPA-400).

Device fabrication:

In a general procedure, indium-tin oxide (ITO)-coated glass substrates were pre-cleaned carefully and treated by UV ozone for 6 min. A 30 nm PEDOT:PSS (Baytron P VP CH 8000) aqueous solution was spin coated onto the ITO substrate and baked at 120 °C for 30 min to remove the residual water. The substrates were then taken into a nitrogen glove box, where the 10 nm cross-linkable hole-transporting layer was spin coated onto the PEDOT:PSS layer from 1,2-dichloroethane solution and annealed at 180 °C for 30 min. The FIrpic-doped PVK:OXD-7 emitting layer was spin coated onto the cross-linkable layer from 1,2-dichloroethane solution and annealed at 100 °C for 30 min. The substrate was then transferred into an evaporation chamber, where the 30 nm TPBi was evaporated at an evaporation rate of 1~2 Å/s under a pressure of 2×10^{-4} Pa and the Cs_2CO_3/Al bilayer cathode was evaporated at evaporation rates of 0.2 and 10 Å/s for Cs_2CO_3 and Al, respectively, under a pressure of 1×10^{-3} Pa. The active area of the device was 9 mm^2. The current–voltage–brightness characteristics of the devices were characterized with Keithley 4200 semiconductor characterization system. The electroluminescent spectra were collected with a Photo Research PR705 Spectrophotometer. All measurements of the devices were carried out in ambient atmosphere without further encapsulations.

Experimental section:

4,4'-(9H,9'H-[3,3'-bicarbazole]-9,9'-diyl)dibenzaldehyde (A)

A mixture of 9H,9'H-3,3'-bicarbazole (3.32 g, 10.0 mmol), 4-bromobenzaldehyde (2.22 g, 12.0 mmol), copper(I) iodide (0.19 g, 1.0 mmol), 1,10-Phenanthroline (0.19 g, 1.0 mmol) and K_2CO_3 (4.2 g, 20.0 mmol) were added to 100 mL of DMF solution and heated at 150 °C for 24 h. After cooling to room temperature, the mixture was poured into water for extraction with ethyl acetate. The organic extracts were washed with water and dried over anhydrous sodium sulfate. After the solvent had been removed, the residue was purified by column chromatography on silica gel with petroleum/dichloromethane (2:1) as the eluent to give the white product (3.6 g, 67 %).^{1}H-NMR (300 MHz, $CDCl_3$): δ 10.13 (s, 2H), 8.18 (dd, *J* = 6.6, 8.1 Hz, 8H), 7.82 (d, *J* = 8.1 Hz, 4H), 7.54 – 7.43 (m, 6H), 7.38 (t, *J* = 7.2 Hz, 4H). ^{13}C-NMR (300 MHz, $CDCl_3$, δ): 193.5, 134.0, 129.5, 128.9, 123.1, 112.37. MS (MALDI-TOF) [m/z]: calcd for $C_{38}H_{24}N_2O_2$, 540.6; found, 540.5. Anal. Calcd. for $C_{38}H_{24}N_2O_2$: C, 84.42; H, 4.47; N 5.18. Found: C, 84.50; H, 4.54; N 5.10.

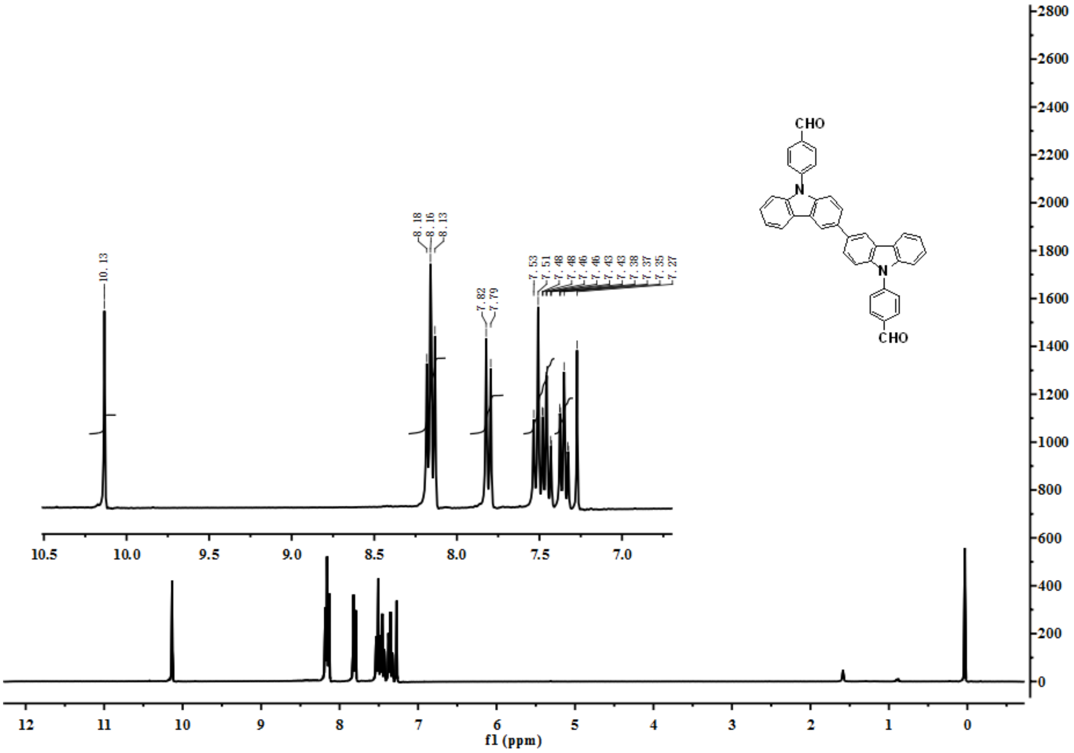
(9H,9'H-[3,3'-bicarbazole]-9,9'-diylbis(4,1-phenylene))dimethanol (B)

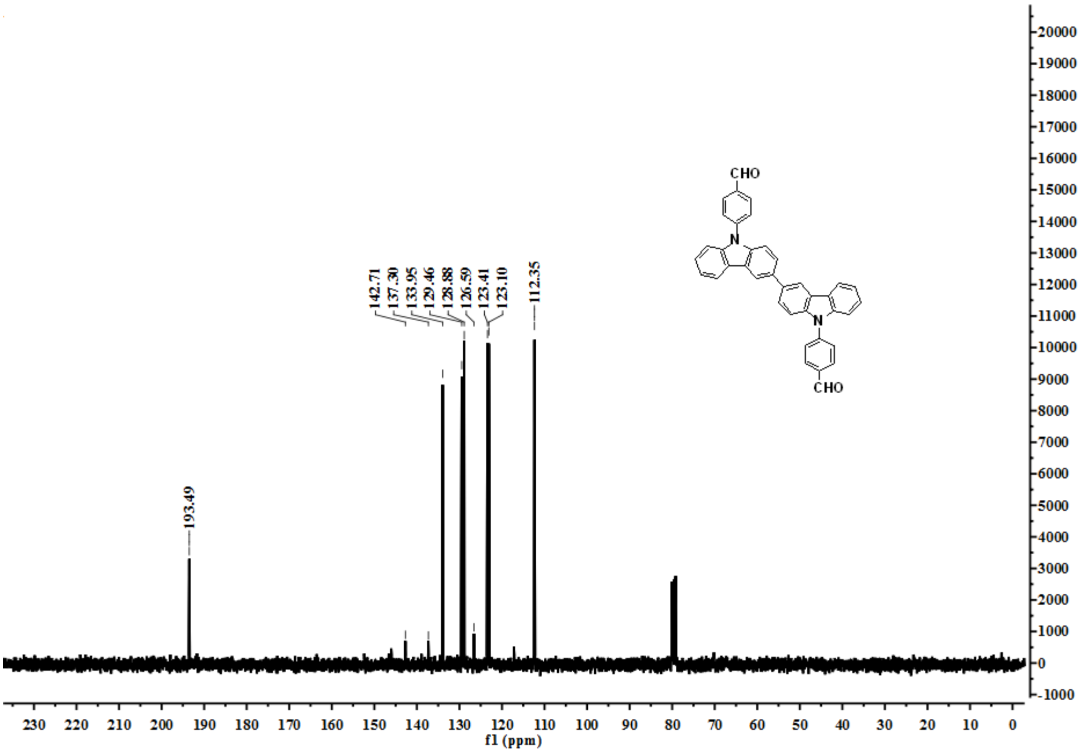
To a solution of compound A (3.6 g, 6.7 mmol) in a mix solvent of THF (50 ml) and ethanol (50 ml) was added $NaBH_4$ (1.27 g, 33.5 mmol) at room temperature for 24h. The solvent was removed by rotary evaporator and then purified by column chromatography (petroleum/ethyl acetate 1:1) to give a white solid (2.92 g, 80%). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.47 (s, 2H), 8.27 (d, *J* = 7.5 Hz, 2H), 7.80 (d, *J* = 8.4 Hz, 2H), 7.67 (t, *J* = 6.3 Hz, 8H),7.52-7.45 (m, 6H), 7.35-7.33 (m, 2H), 4.87 (s, 4H). ^{13}C-NMR (300 MHz, $CDCl_3$, δ): 144.0, 142.7, 139.7, 137.0, 131.1, 129.8, 128.7, 128.5, 126.6, 126.2, 123.1, 122.7, 121.5, 112.6, 112.5, 67.5. MS (MALDI-TOF) [m/z]: calcd for $C_{38}H_{28}N_2O_2$, 544.6; found, 544.6. Anal. Calcd. for $C_{38}H_{28}N_2O_2$: C, 83.80; H, 5.18; N 5.14. Found: C, 83.75; H, 5.20; N 5.16.

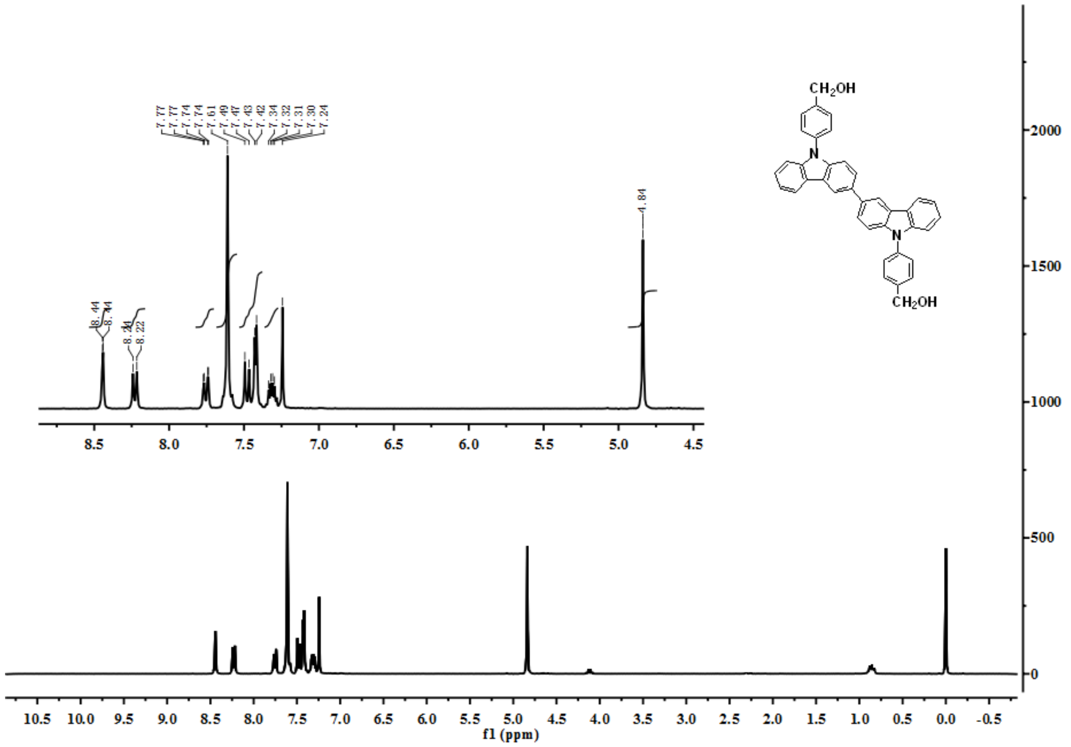
9,9'-bis(4-(((4-vinylbenzyl)oxy)methyl)phenyl)-9H,9'H-3,3'-bicarbazole (BCz-VB)

To a solution of compound B (2.92 g, 5.36 mmol) in DMF (50 ml) was added sodium hydride (0.54 g, 21.44 mmol) at room temperature for 1h. Then, 4-vinylbenzyl chloride (3.8 g, 25.0 mmol) was added to the solution, and the mixture was stirred for 12h. After the reaction finished, the reaction mixture was extracted with dichloromethane and water. The organic layer was dried by anhydrous $MgSO_4$ and filtered. The product was isolated by silica gel column chromatography using petroleum ether/ethyl acetate (10:1) eluent to afford a white solid (2.90 g, 45 %).^{1}H-NMR (300 MHz, $CDCl_3$, δ): 8.47 (s, 2H), 8.27 (d, *J* = 7.5 Hz , 2H), 7.81 (d, *J* = 8.7 Hz, 2H), 7.67 (t, *J* = 9.0 Hz, 8H), 7.54-7.44 (m, 14H), 7.36-7.33 (m, 2H), 6.82 (dd, *J* = 10.8, 17.7 Hz, 2H), 5.83 (d, *J* = 17.4 Hz, 2H), 5.30 (d, *J* = 10.8 Hz , 2H), 4.70 (s, 8H). ^{13}C-NMR (300 MHz, $CDCl_3$, δ): 144.0, 142.6, 140.3, 139.8, 139.1, 137.0, 131.9, 130.7, 129.7, 129.0, 128.7, 128.4, 126.6, 126.2, 123.0, 122.6, 121.5, 116.5, 112.6, 75.0, 74.3. MS (MALDI-TOF) [m/z]: calcd for $C_{56}H_{44}N_2O_2$, 776.9;

found, 777.0. Anal. Calcd. for $C_{56}H_{44}N_2O_2$: C, 86.57; H, 5.71; N 3.61. Found: C, 86.60; H, 5.65; N 3.60.



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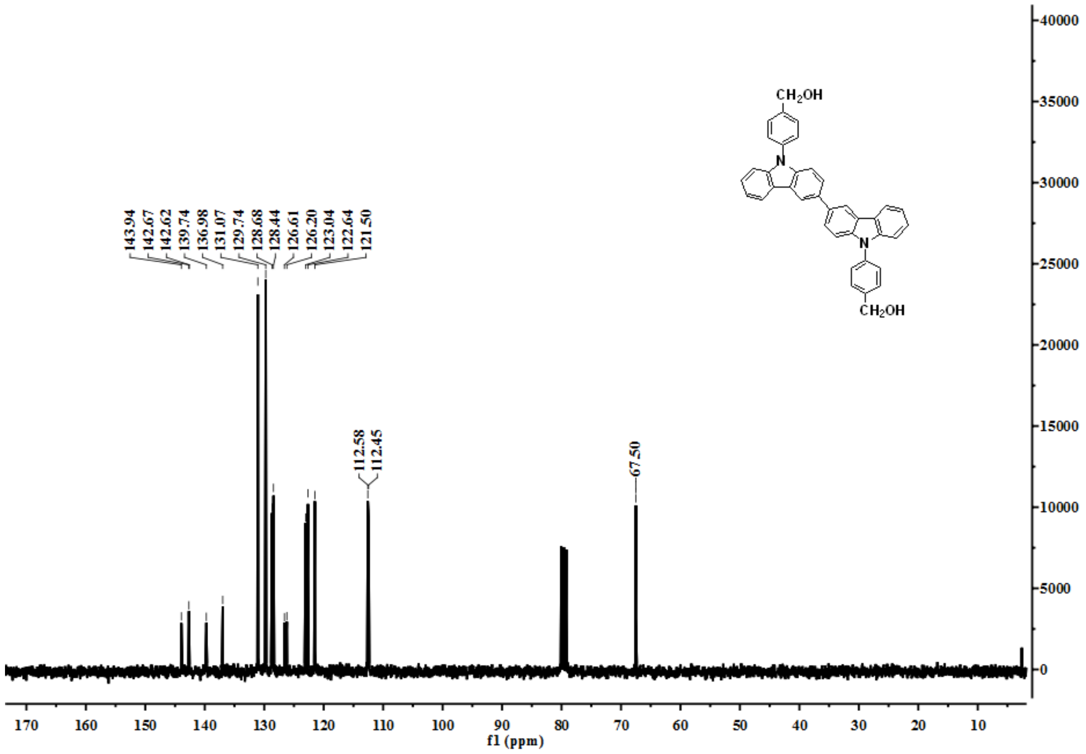
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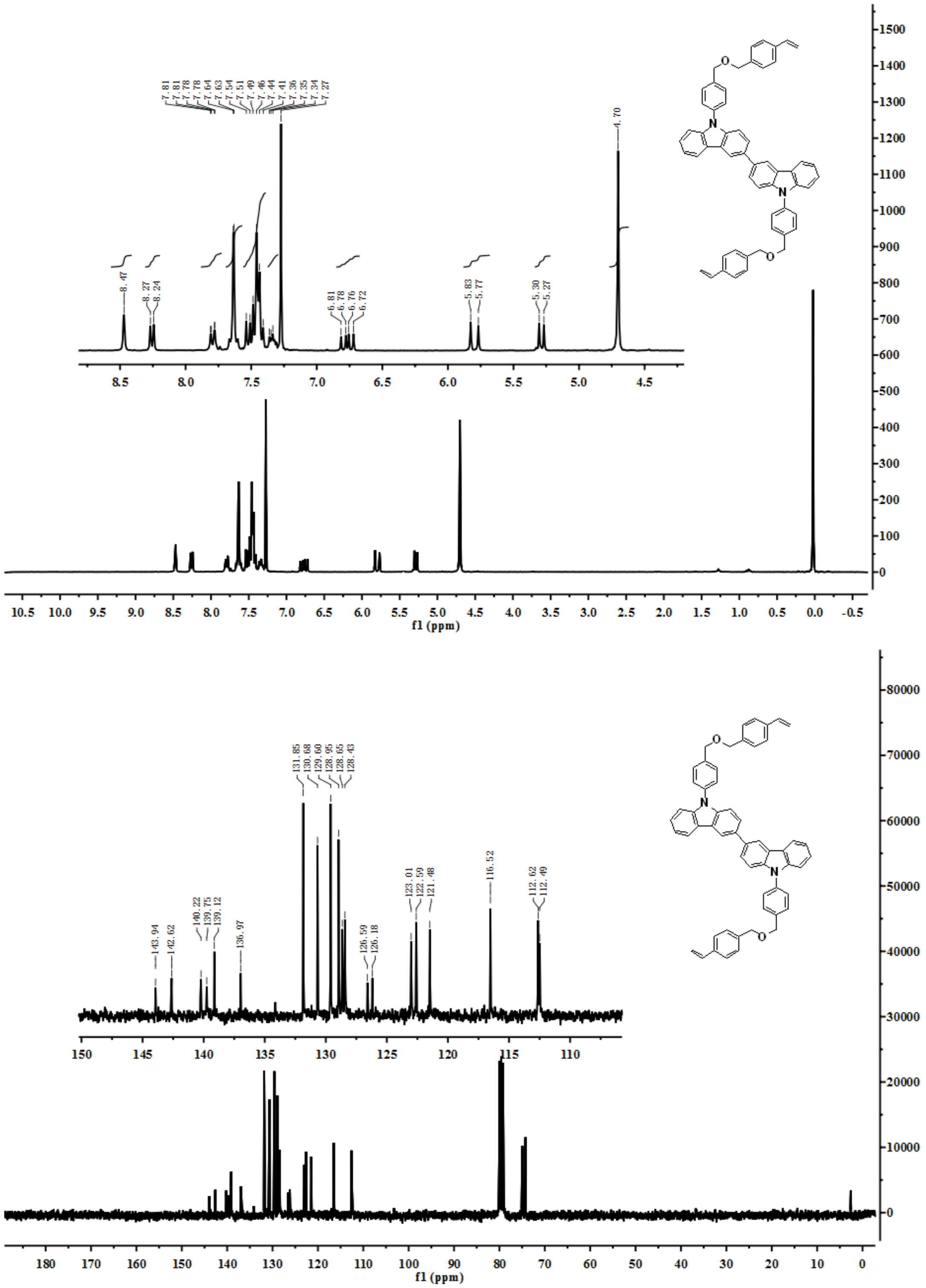


Figure S1. ^{1}H-NMR and ^{13}C-NMR of compound A, B and DCz-VB.

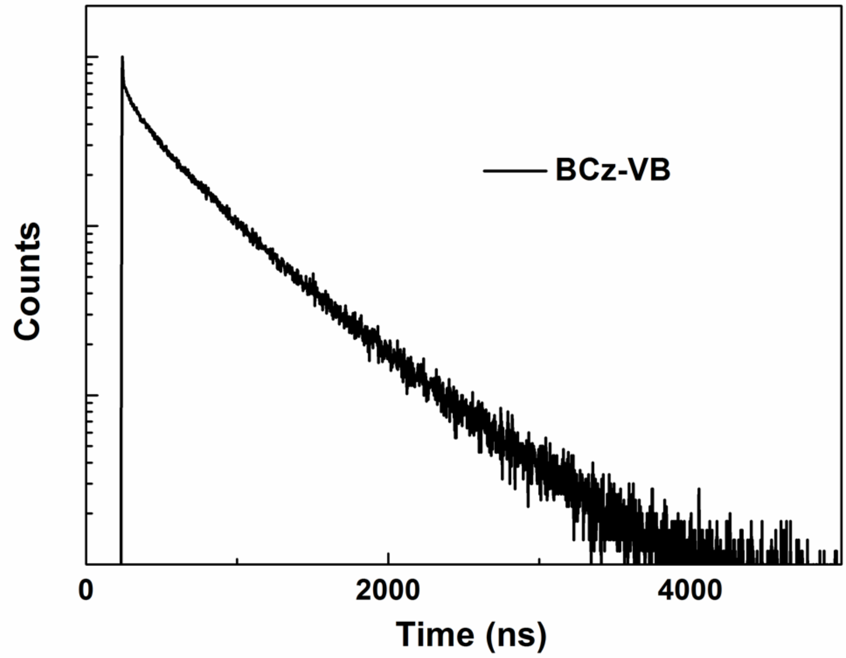
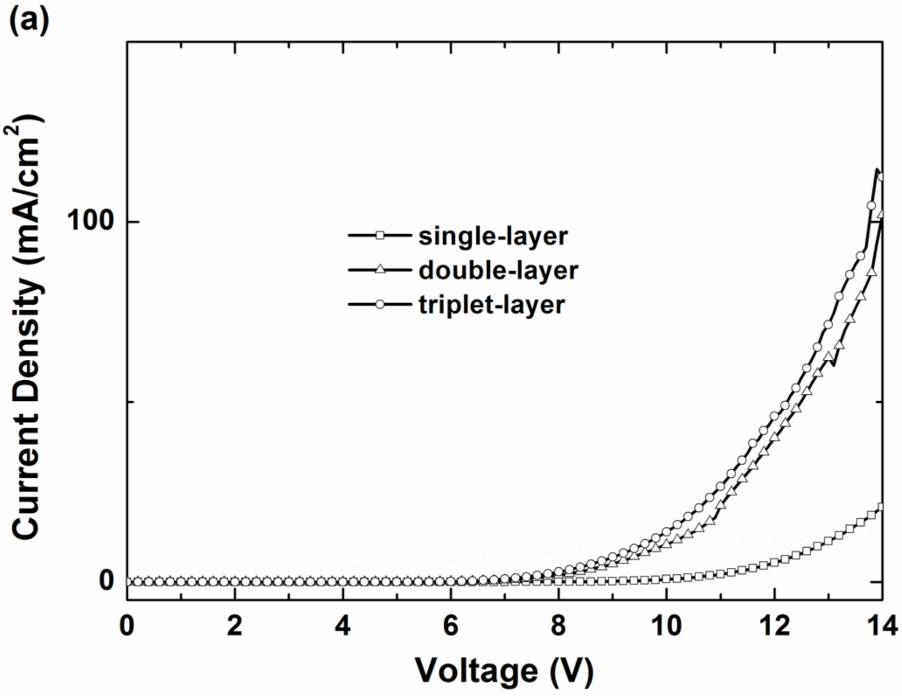


Figure S2. Transient photoluminescence decay curve of FIrpic-doped films monitored at 470.



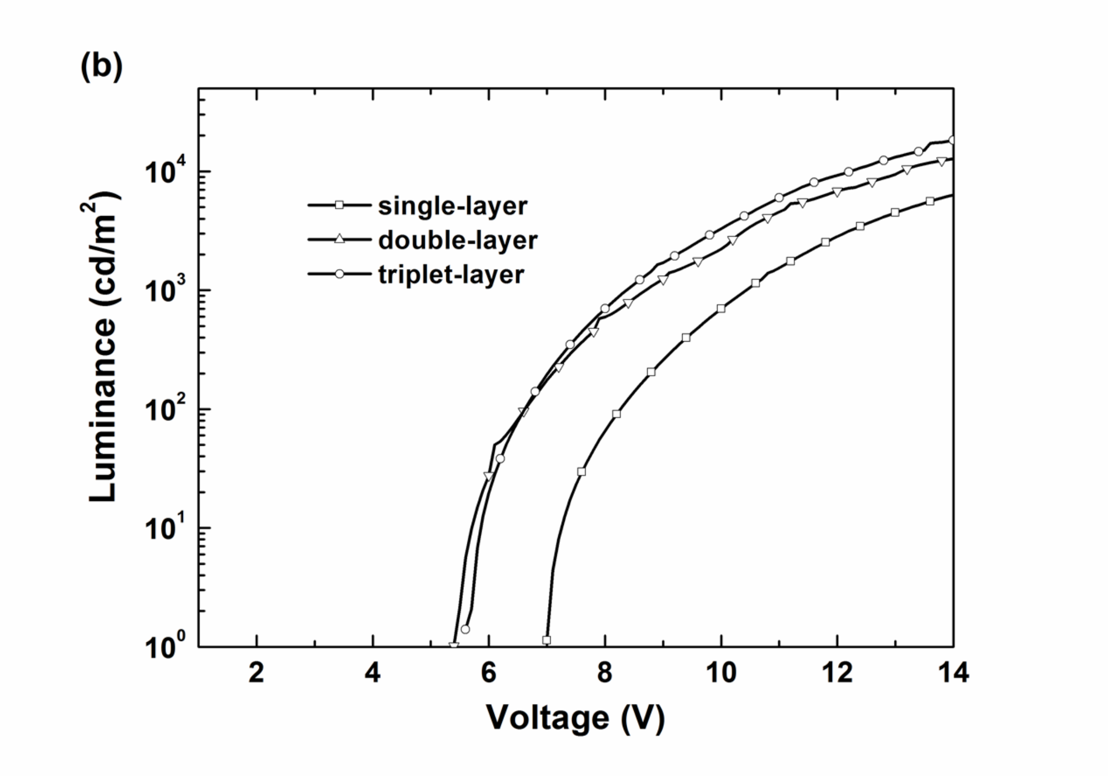


Figure S3. *I-V-L* characteristics of BCz-VB based devices.