

## Supplementary Information

### **Bicarbazole-triazine hybrid typed mixed host materials for blue phosphorescent OLEDs with enhanced efficiency and lifetime**

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## Synthesis and characterizations of molecules

### 9-phenyl-9H-2,9'-bicarbazole (PH1)

A solution of SPhos (2.04 g, 4.97 mmol) in xylene (50 mL) was added to a mixture of 2-bromo-9-phenyl-9H-carbazole (8.0 g, 24.83 mmol), carbazole (4.57 g, 27.31 mmol), sodium tert-butoxide (4.77 g, 49.66 mmol), and  $[\text{Pd}_2(\text{dba})_3]$  (2.27 g, 2.48 mmol) in xylene (100 mL). After heating under argon at 150 °C for overnight, the reaction mixture was concentrated, and purification by silica-gel column chromatography afforded product (9.1 g, 90%)

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 8.33 (d, 1H,  $J = 8$  Hz), 8.22 (d, 1H,  $J = 7.6$  Hz), 8.14 (d, 2H,  $J = 8$  Hz), 7.57 – 7.53 (m, 5H), 7.46 – 7.34 (m, 9H), 7.29 – 7.25 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 141.7, 141.6, 141.4, 137.2, 135.5, 130.1, 127.8, 126.9, 126.4, 125.9, 123.2, 122.9, 122.7, 121.4, 120.5, 120.4, 120.3, 119.7, 119.3, 110.0, 109.8, 108.7. Q-TOF MS (mass  $m/z$ ): calculated for  $\text{C}_{30}\text{H}_{20}\text{N}_2$ : 408.1626, Found: 409.1644  $[\text{M}+\text{H}]^+$ .

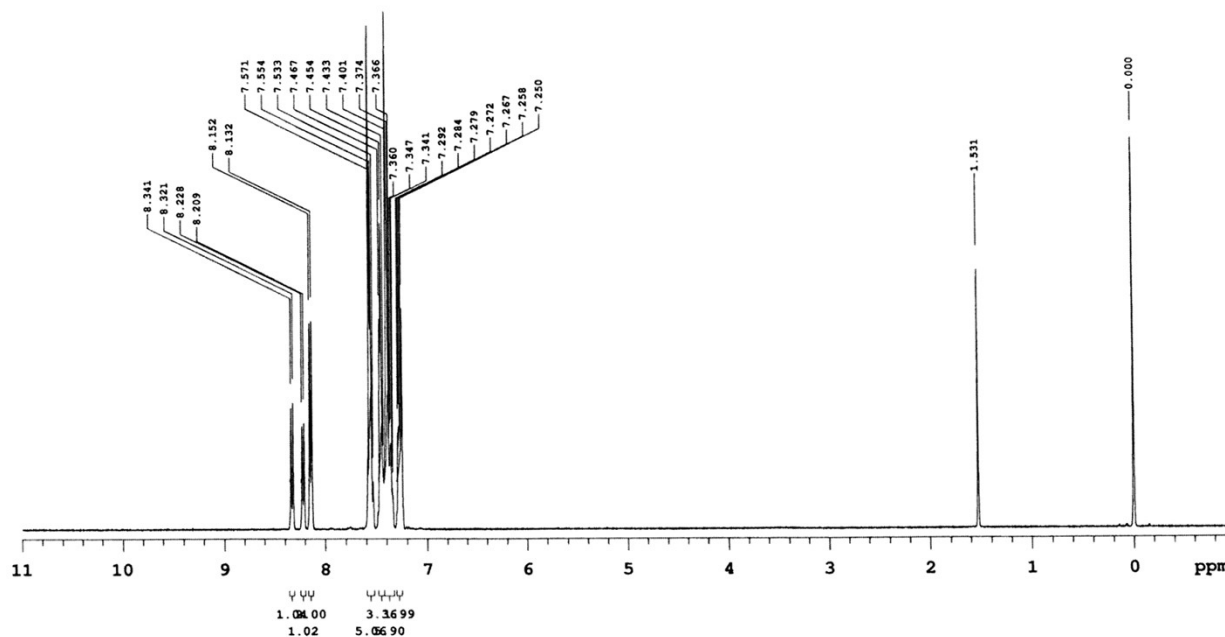


Figure S1.  $^1\text{H}$ -NMR spectrum of PH1

## 9-(4-(triphenylsilyl)phenyl)-9H-3,9'-bicarbazole (PH2)

A solution of SPhos (1.73 g, 4.21 mmol) in xylene (50 mL) was added to a mixture of 3,9'-Bicarbazole (7.0 g, 21.06 mmol), (4-bromophenyl)triphenylsilane (9.72 g, 23.16 mmol), sodium tert-butoxide (4.05 g, 42.12 mmol), and  $[\text{Pd}_2(\text{dba})_3]$  (1.93 g, 2.11 mmol) in xylene (100 mL). After heating under argon at 150 °C for overnight, the reaction mixture was concentrated, and purification by silica-gel column chromatography afforded product (12.1 g, 86%)

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 8.28 (s, 1H), 8.18 (d, 2H,  $J = 7.2$  Hz), 8.10 (d, 1H,  $J = 8$  Hz), 7.68 – 7.65 (m, 10H), 7.56 – 7.53 (m, 2H), 7.50 – 7.38 (m, 15H), 7.33 – 7.29 (m, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 141.8, 141.3, 139.7, 138.6, 138.1, 136.4, 134.2, 133.7, 130.0, 129.9, 128.1, 126.7, 126.2, 125.8, 125.5, 124.5, 123.1, 123.0, 120.6, 120.5, 120.2, 119.6, 119.4, 111.0, 110.3, 109.8. Q-TOF MS (mass  $m/z$ ): calculated for  $\text{C}_{48}\text{H}_{34}\text{N}_2\text{Si}$ : 666.2491, Found: 667.2482  $[\text{M}+\text{H}]^+$ .

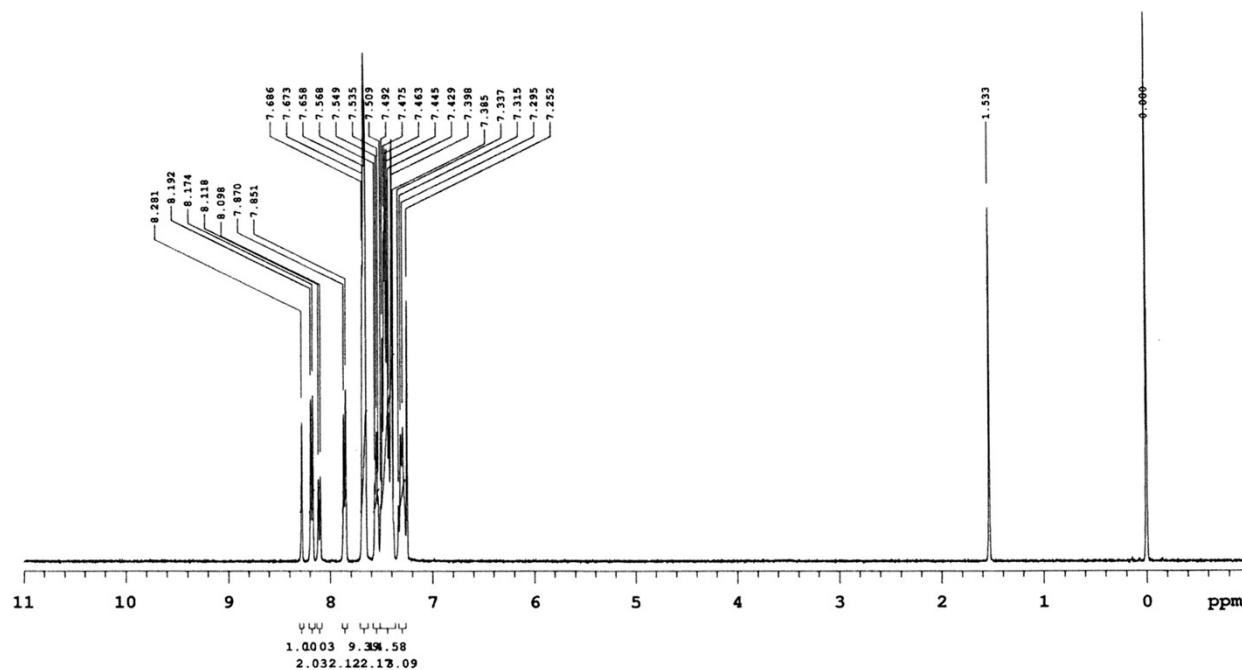


Figure S2.  $^1\text{H}$ -NMR spectrum of PH2

### 9-(3-(triphenylsilyl)phenyl)-9H-3,9'-bicarbazole (PH3)

A solution of SPhos (1.48 g, 3.6 mmol) in xylene (50 mL) was added to a mixture of 3,9'-Bicarbazole (6.0 g, 18.05 mmol), (3-bromophenyl)triphenylsilane (8.33 g, 19.86 mmol), sodium tert-butoxide (3.47 g, 36.1 mmol), and  $[\text{Pd}_2(\text{dba})_3]$  (1.65 g, 1.8 mmol) in xylene (100 mL). After heating under argon at 150 °C for overnight, the reaction mixture was concentrated, and purification by silica-gel column chromatography afforded product (11.2 g, 80%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 8.26 (s, 1H), 8.20 (d, 2H,  $J = 8$  Hz), 8.09 (d, 1H,  $J = 8$  Hz), 7.87 (s, 1H), 7.76 – 7.64 (m, 9H), 7.57 – 7.40 (m, 17H), 7.33 – 7.30 (m, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 141.8, 141.3, 139.7, 137.4, 137.0, 136.4, 136.3, 135.4, 134.4, 133.5, 129.9, 129.8, 129.6, 128.1, 128.0, 127.8, 126.6, 125.8, 125.4, 124.4, 123.1, 122.9, 120.5, 120.4, 120.3, 119.6, 119.4, 110.9, 110.1, 109.8. Q-TOF MS (mass  $m/z$ ): calculated for  $\text{C}_{48}\text{H}_{34}\text{N}_2\text{Si}$ : 666.2491, Found: 667.2471  $[\text{M}+\text{H}]^+$ .

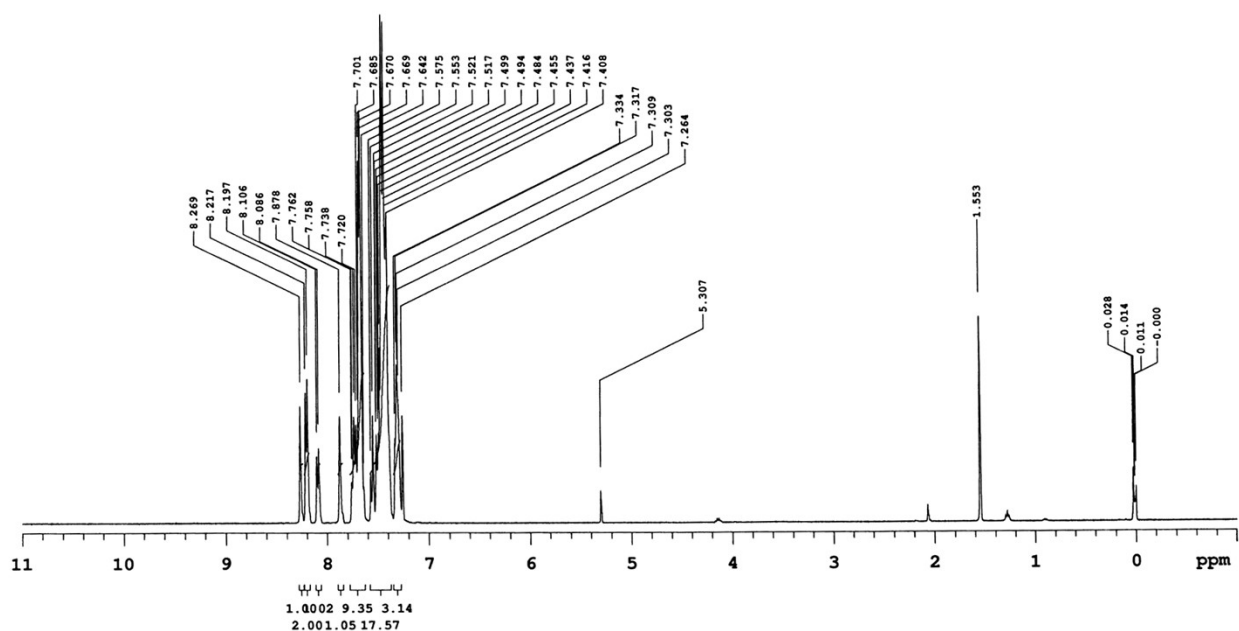


Figure S3.  $^1\text{H}$ -NMR spectrum of PH3



### 9'-phenyl-9'H-9,3':6',9''-tercarbazole (PH4)

A solution of tert-butyl phosphine (1.01 g, 4.99 mmol) in xylene (50 mL) was added to a mixture of 3,6-dibromo-9-phenyl-9H-carbazole (10.0 g, 24.93 mmol), carbazole (9.17 g, 54.85 mmol), sodium tert-butoxide (11.98 g, 124.66 mmol), and  $[\text{Pd}_2(\text{dba})_3]$  (2.28 g, 2.49 mmol) in xylene (100 mL). After heating under argon at 150 °C for overnight, the reaction mixture was concentrated, and purification by silica-gel column chromatography afforded product (6.0 g, 42%)

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 8.27 (s, 2H), 8.15 (d, 4H,  $J = 8$  Hz), 7.74 – 7.55 (m, 9H), 7.42 – 7.38 (m, 8H), 7.30 – 7.24 (m, 4H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 141.8, 140.7, 137.1, 130.3, 130.2, 128.2, 127.2, 126.2, 125.9, 123.9, 123.1, 120.3, 119.7, 119.8, 111.3, 109.7. Q-TOF MS (mass  $m/z$ ): calculated for  $\text{C}_{42}\text{H}_{27}\text{N}_3$ : 573.2205, Found: 574.2206  $[\text{M}+\text{H}]^+$ .

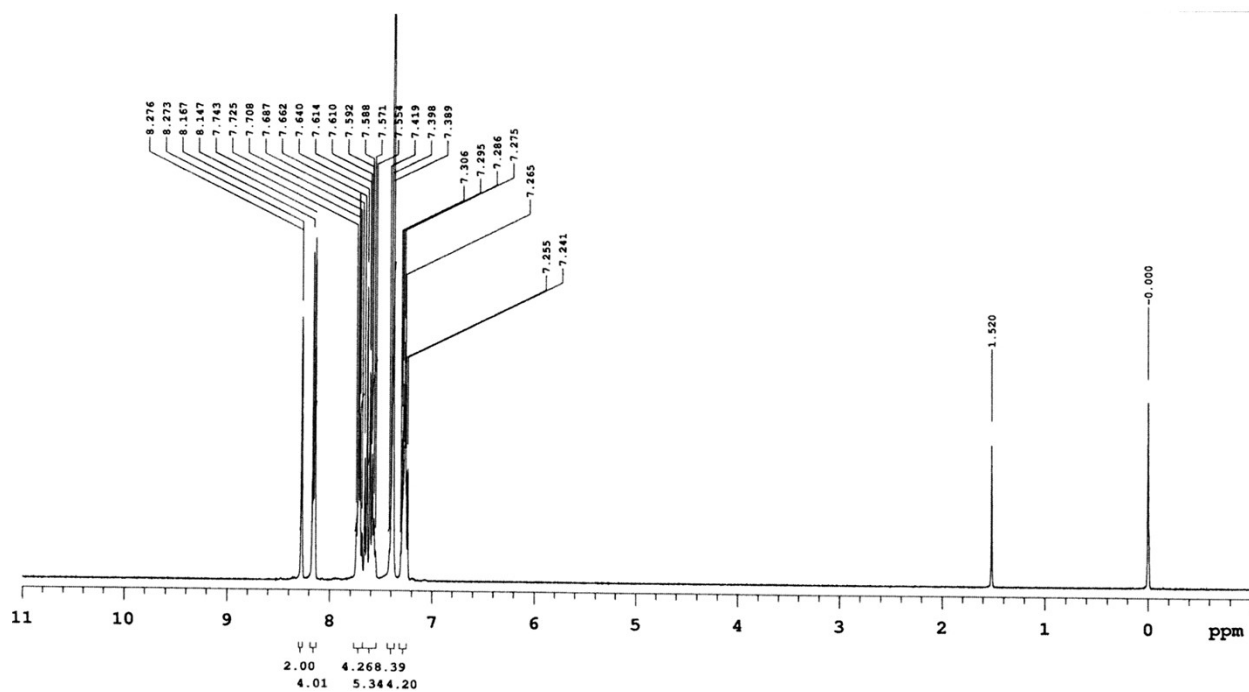


Figure S4.  $^1\text{H}$ -NMR spectrum of PH4

## 9-(4,6-diphenyl-1,3,5-triazin-2-yl)-9'-phenyl-9H,9'H-4,4'-bicarbazole (PH5)

A solution of XPhos (1.42 g, 2.99 mmol) in xylene (100 mL) was added to a mixture of 4-(9H-carbazol-4-yl)-9-phenyl-carbazole (12.2 g, 29.87 mmol), 2-chloro-4,6-diphenyl-1,3,5-triazine (11.99 g, 44.80 mmol), sodium tert-butoxide (5.74 g, 58.54 mmol), and  $[\text{Pd}_2(\text{dba})_3]$  (1.37 g, 1.49 mmol) in xylene (100 mL). After heating under argon at 150 °C for 12 h, the reaction mixture was concentrated, and purification by silica-gel column chromatography afforded product (14.0 g, 72%)

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 9.36 (d, 1H,  $J = 8.4$  Hz), 9.11 (d, 1H,  $J = 8.8$  Hz), 8.81 (d, 4H,  $J = 8.8$  Hz), 7.77 (t, 1H,  $J = 8$  Hz), 7.67 – 7.64 (m, 10H), 7.56 (d, 2H,  $J = 3.6$  Hz), 7.52 (d, 2H,  $J = 7.6$  Hz), 7.41 (t, 1H,  $J = 7.8$  Hz), 7.36 – 7.34 (m, 2H), 7.23 (t, 1H,  $J = 8$  Hz), 6.93 (d, 2H,  $J = 7.6$  Hz), 6.86 (d, 1H,  $J = 7.6$  Hz), 6.81 (t, 1H,  $J = 7.4$  Hz);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 172.5, 165.3, 141.3, 141.2, 139.5, 139.3, 137.7, 136.3, 135.5, 135.3, 132.8, 129.9, 129.2, 128.9, 127.7, 127.5, 126.8, 126.6, 126.4, 125.9, 125.7, 124.9, 124.5, 123.1, 123.0, 122.2, 122.1, 121.5, 121.3, 119.8, 118.9, 116.7, 109.4, 109.2, Q-TOF MS (mass  $m/z$ ): calculated for  $\text{C}_{45}\text{H}_{29}\text{N}_5$ : 639.2423, Found: 640.2416  $[\text{M}+\text{H}]^+$ .

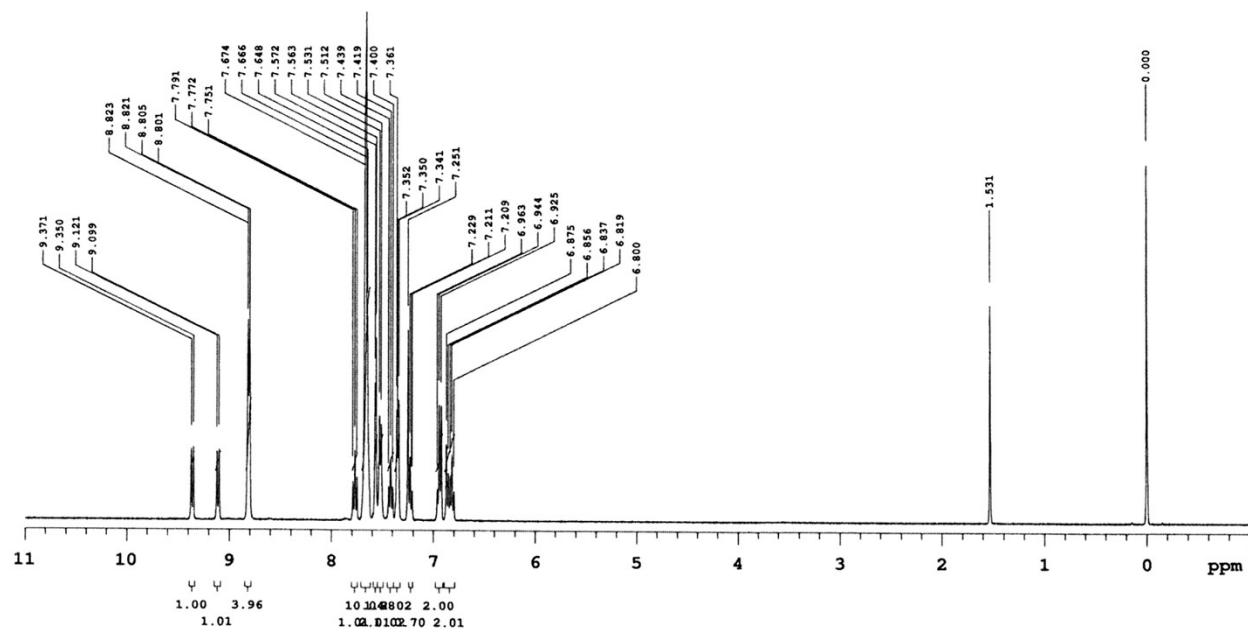
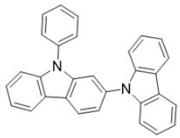
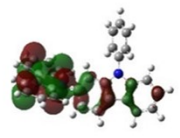
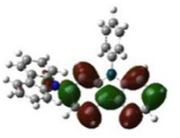
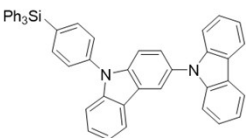
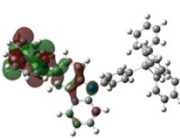
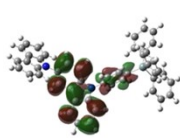
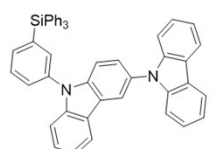
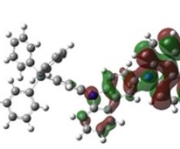
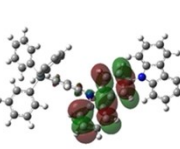
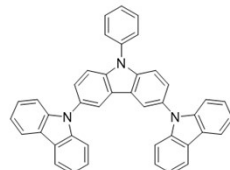
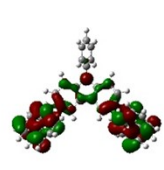
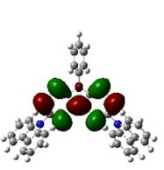
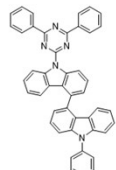
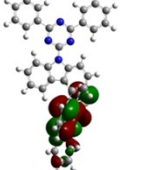
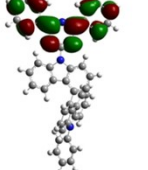
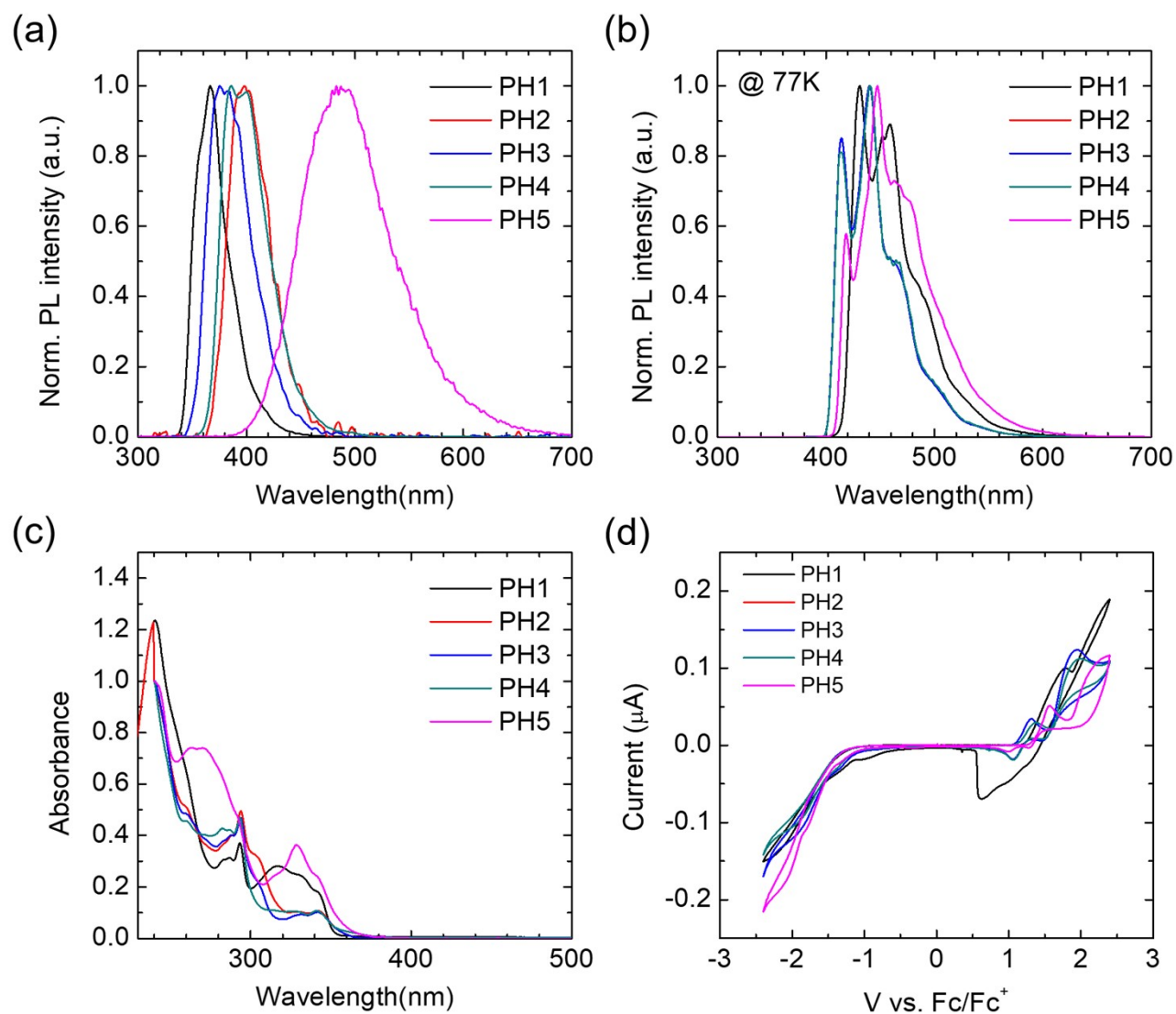


Figure S5.  $^1\text{H}$ -NMR spectrum of PH5

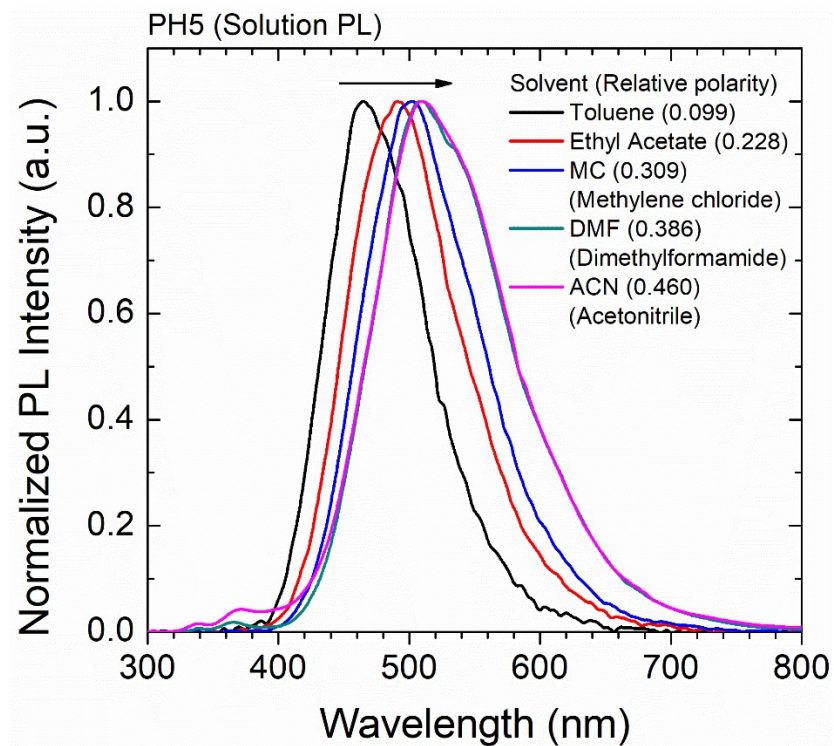
Name	Molecular structure	HOMO	Band gap	LUMO
PH1		-5.57 (eV) 	4.16	-1.41 (eV) 
PH2		-5.52 (eV) 	4.13	-1.39 (eV) 
PH3		-5.50 (eV) 	4.13	-1.37 (eV) 
PH4		-5.56 (eV) 	3.93	-1.63 (eV) 
PH5		-5.66 (eV) 	3.42	-2.25 (eV) 

**Figure S6.** DFT calculation results on five different molecules.





**Figure S7.** PL spectra of **PH1-PH5** (a) at room temperature, (b) at 77 K in 2-Me-THF. (c) Absorption spectra in 2-Me-THF. (d) CV curves of **PH1-PH5** in dichloromethane solution containing 0.1 M  $n\text{-Bu}_4\text{PF}_6$  as an electrolyte, at a scan rate of  $0.1 \text{ V s}^{-1}$ .



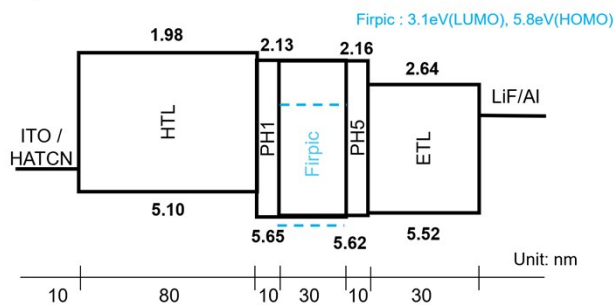
**Figure S8.** PL spectra of **PH5** in various kinds of solvents with different relative polarity values. As the polarity of the solvent decreases, the PL spectrum is getting closer to the one using a thin film, shown in Figure 2.

## **Device fabrication and characterization**

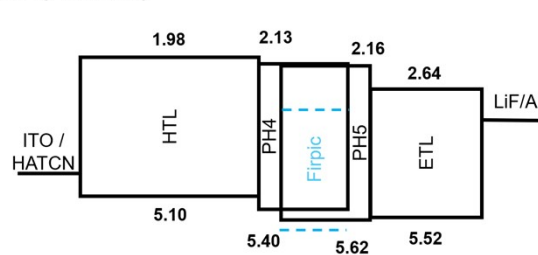
**Device fabrication.** PhOLEDs were fabricated in a thermal evaporator. The base pressure was kept under  $5 \times 10^{-7}$  Torr to make a smooth thin film on a substrate. The indium-tin-oxide pre-patterned glass substrates were cleaned in acetone and IPA using a sonication bath for 10 minutes each. Then, the cleaned substrates were treated in a UV-Ozone machine for 15 minutes. After transferring the substrates, organic layers are sequentially deposited with a shadow mask at a 0.1 nm/s rate. We moved the sample from the organic chamber to the metal chamber without breaking the vacuum for the Al metal electrode. The evaporation rate was kept at 0.3 nm/s for Al. Before the measurement, we did an encapsulation process using an epoxy resin and glass caps inside a glove box filled with N<sub>2</sub> gas.

**Optoelectrical characterization.** The optoelectrical characteristics of PhOLEDs were tested using a semiconductor parameter analyzer (Keithley 237) connected with a spectrophotometer (Photo Research PR-670). The transient EL intensity was detected using a pulse generator (Agilent 8114A) and a spectrometer (SpectraPro-300i) connected to a photomultiplier tube (Acton Research, PD-438). The detection wavelength was 470 nm, corresponding to the peak wavelength of the emitter. All signals were integrated more than 1000 times using an oscilloscope (Agilent 54642A). The voltage was measured over a 1 M $\Omega$  resistance that was parallel to PhOLEDs. The C-V curves were measured on a probe station using a parameter analyzer (Keithley 4200).

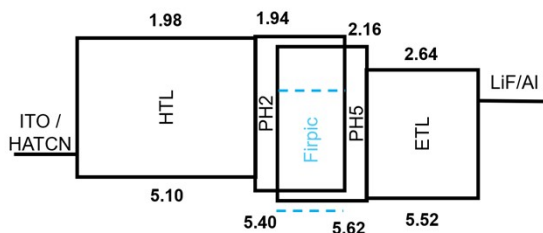
※ D1 (PH1:PH5)



※ D2 (PH4:PH5)



※ D3 (PH2:PH5)



※ D4 (PH3:PH5)

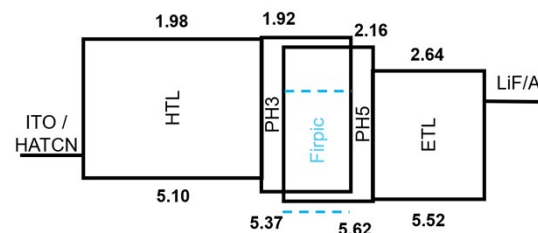
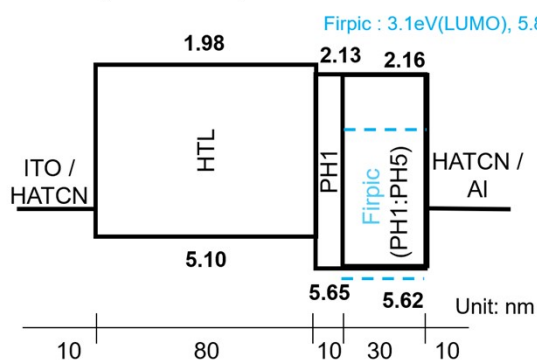
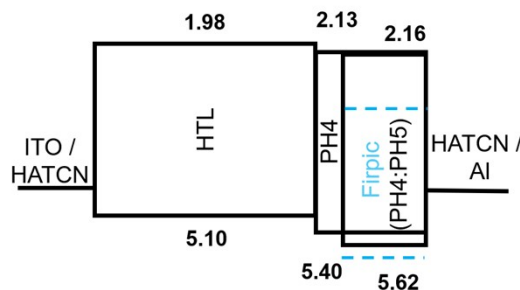


Figure S9. Schematic diagrams of the structures of the blue PhOLEDs.

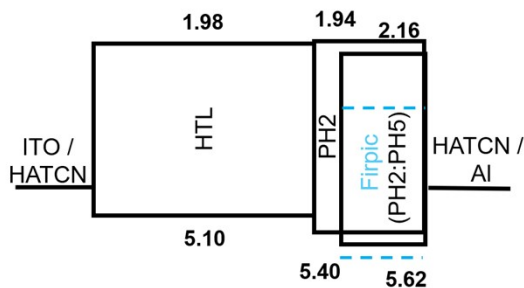
※ HOD for D1(PH1 : PH5)



※ HOD for D2(PH4:PH5)



※ HOD for D3(PH2:PH5)



※ HOD for D4(PH3:PH5)

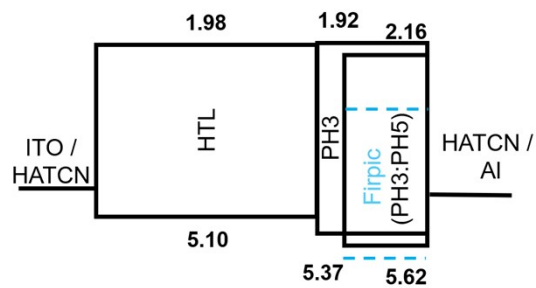
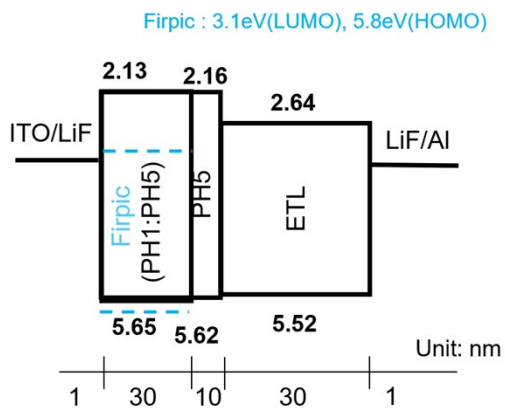
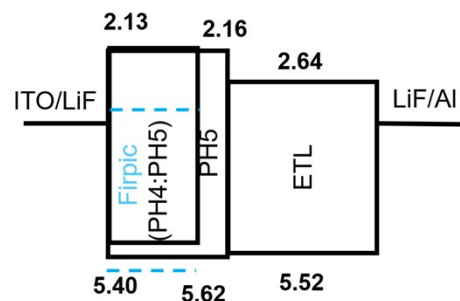


Figure S10. Schematic diagrams of the structures of hole-only devices (HODs).

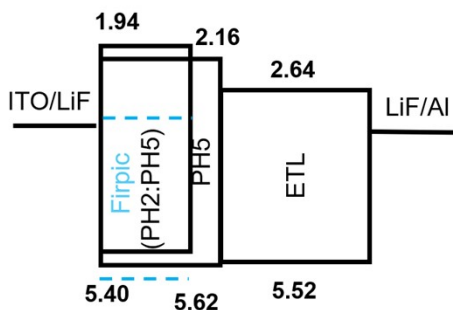
※ EOD for D1(PH1 : PH5)



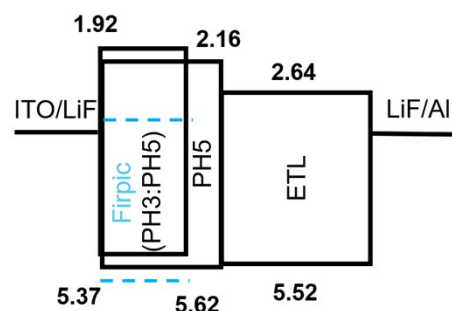
※ EOD for D2(PH4:PH5)



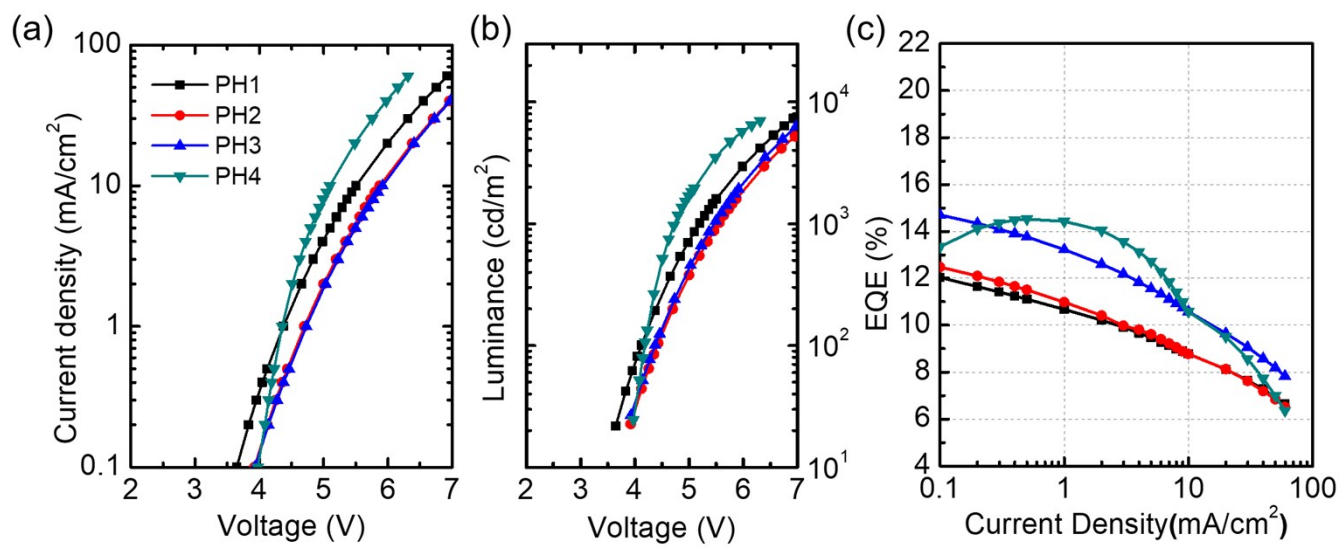
※ EOD for D3(PH2:PH5)



※ EOD for D4(PH3:PH5)



**Figure S11.** Schematic diagrams of the structures of electron-only devices (EODs).



**Figure S12.** The performance of PhOLEDs using a single host.