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A universal host material with simple structure for monochrome and white phosphorescent/TADF OLEDs

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General Information

All chemicals, reagents, and solvents were used as received from commercial sources without further purification. All reactions were carried out under nitrogen and anhydrous conditions unless noted otherwise. ¹H NMR (400MHz) and ¹³C NMR (100 MHz) spectra were measured on a Bruker Ascend 400 spectrometer using CDCl₃ as a solvent and the spectral data were reported in ppm relative to tetramethylsilane (TMS) as an internal standard. Molecular weights were measured with a Bruker Autoflex III MALDI-TOF mass spectrometer. Elemental analyses of carbon, hydrogen, and nitrogen were performed on a Vario EL III microanalyzer. UV-vis absorption spectra were recorded on a PG TU-1901 recording spectrophotometer. Photoluminescence (PL) spectra were measured on a Hitachi F-7000 fluorescence spectrophotometer and phosphorescence spectra at 77 K were recorded on a Perkin-Elmer LS 50B spectrofluorometer. The absolute PL quantum yields were measured using a Hamamatsu C9920-02G integrating sphere system coupled with a 150 W xenon lamp and a PMA-12 photonic multichannel analyzer. Film morphology was characterized by polarizing optical microscopy (Leica DMLP) and recorded with a digital camera. Differential scanning calorimetry (DSC) was performed on a Mettler Toledo DSC1 STARe system with nitrogen flow at 20 ml/ min. Samples were preheated to above their melting points, and then cooled down to -30 °C at -100 °C/min before the second heating and cooling scans were recorded at 10 °C/min. Thermogravimetric analysis (TGA) was undertaken with a TA instrument Q600 at a scanning rate of 10 °C/min under nitrogen. Cyclic voltammetry (CV) was carried out using nitrogenpurged anhydrous tetrahydrofuran (THF) for the reduction and dichloromethane for the oxidation scan at room temperature with a CHI voltammetric analyzer. Tetrabutylammonium hexafluorophosphate (TBAPF₆) (0.1 M) was used as the supporting electrolyte. The conventional three-electrode configuration consists of a platinum working electrode, a platinum wire auxiliary electrode, and an Ag wire pseudo-reference electrode with ferrocenium–ferrocene (Fc⁺/Fc) as the internal standard. Cyclic voltammograms were obtained at a scan rate of 100 mV/s. Formal potentials are calculated as the average of cyclic voltammetric anodic and cathodic peaks. The onset potential was determined from the intersection of two tangents drawn at the rising and background current of the cyclic voltammogram. The geometrical and electronic properties of the three hosts were performed with the Gaussian 09 program package. The calculation was optimized by means of B3LYP with the 6-31G(d) atomic basis set. The molecular orbitals were visualized using Gaussview.

Synthesis of Materials

N,N-Diphenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline. 4-Bromo-N,Ndiphenylaniline (3.24 g, 10.0 mmol), bis(pinacolato)diboron (3.175 g, 12.5 mmol), CH₃COOK (2.94 g, 30.0 mmol), and Pd(dppf)Cl₂ (0.2196 g, 0.3 mmol) were dissolved in 1,4-dioxane (60 mL) under nitrogen atmosphere. The reaction mixture was stirred and refluxed for 24 h. After cooling, the mixture was evaporated under reduced pressure, treated with saturated sodium chloride solution and extracted with dichloromethane. The organic layer was dried over anhydrous MgSO₄ and solvent was removal under reduced pressure yielded brown viscous oil. It was purified by column chromatography on silica gel using ethyl acetate/petroleum ether at 1:30 by volume as the eluent to give a white powder. Yield: 97%. ¹H NMR (400 MHz, CDCl₃, δ): 7.66 (d, J = 8.4 Hz, 2H), 7.25 (t, J = 7.8 Hz, 4H), 7.10 (d, J = 7.9 Hz, 4H), 7.03 (t, J = 7.7 Hz, 4H), 1.33 (s, 12H).

4'-(*Diphenylamino*)-[1,1'-biphenyl]-4-carbonitrile (TPA-BN). N,N-Diphenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (1.6 g, 4.3 mmol), anhydrous sodium carbonate (4.8 g, 45.3 mmol), p-bromobenzonitrile (0.75 g, 4.1 mmol), and Pd(PPh₃)₄ (0.13 g, 0.1125 mmol) were dissolved in 60 mL of toluene and 25 mL of oxygen-free water and then stirred at a temperature of 90 °C under nitrogen atmosphere for 24 hours. After cooling, extracted with chloroform, washed with water, and the organic layer was dried over anhydrous MgSO₄. After removal of the solvent, the residue was purified by column chromatography on silica gel using ethyl acetate/petroleum ether at 1:10 by volume as the eluent to give a white powder. Yield: 94%. ¹H NMR (400 MHz, CDCl₃, δ): 7.67 (dd, J = 8.4, 8.5 Hz, 4H), 7.46 (d, J = 8.7Hz, 2H), 7.29 (dd, J = 8.7, 6.7 HZ, 4H), 7.14 (dd, J = 8.2, 6.8 Hz, 6H), 7.08 (t, J = 7.3 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃, δ): 147.54, 146.23, 144.00, 131.54, 131.09, 128.40, 126.83, 125.89, 123.91, 122.55, 121.97, 118.06, 109.04. MALDI-TOF-MS: 346.36. Anal. calcd for C₂₅H₁₈N₂ (%): C 86.68, H 5.24, N 8.09; found: C 86.77, H 5.47, N 8.02.

4-Ally-N,N-diphenylaniline. 4-Bromo-N,N-diphenylaniline (1.90 g, 5.9 mmol), anhydrous potassium fluoride (3.30 g, 56.8 mmol), Pd(PPh₃)₄ (0.2984 g, 0.26 mmol)

and allyltributyltin (5.5 mL) were dissolved in 1,4-dioxane (60 mL) under nitrogen atmosphere. The reaction mixture was stirred at a temperature of 100 °C and refluxed for 24 h. After cooling, the mixture was poured into ammonia solution (the volume ratio of ammonia to water is 1:2) and stirred for 0.5 h, extracted with chloroform and washed with water. The organic layer was dried over anhydrous MgSO₄ and then filtered. Evaporation of the solvent under reduced pressure afforded the crude solid. It was purified by column chromatography on silica gel using ethyl acetate/petroleum ether at 1:15 by volume as the eluent to give a pale yellow powder. Yield: 67%. ¹H NMR (400 MHz, CDCl3, δ): 7.21 (dd, *J* = 14.7, 6.4, 4H), 7.07-6.94 (m, 10H), 5.97 (ddt, *J* = 16.8, 10.0, 6.7, 1H), 5.11-5.05 (m, 3H), 3.34 (d, *J* = 6.7, 1H).

4-(3-(4-(Diphenylamino)phenyl)propyl)benzonitrile (TPA-L-BN). 9-BBN (0.5 M in THF, 14.54 mL, 7.27 mmol) was added dropwise into a solution of 4-ally-N,N-diphenylaniline (0.69 g, 2.42 mmol) in THF (30 mL) at 0 °C. The mixture was stirred at room temperature for 15 min and then at 35 °C for 3 h before transferring into a mixture of p-bromobenzonitrile (0.62 g, 3.4 mmol), Pd(PPh₃)₄ (0.08 g, 0.069 mmol), Na₂CO₃ (11 g, 103.0 mmol), H₂O (52 mL) and toluene (86 mL). The reaction mixture was stirred at 90 °C for 24 h, cooled down to room temperature, and extracted with chloroform. The organic extracts were combined, washed with water, and dried over anhydrous MgSO₄. Upon evaporating off the solvent, the crude product was purified by column chromatography on silica gel with ethyl acetate/petroleum ether at 1:20 by volume as the eluent to give a white powder. Yield: 84%. ¹H NMR (400 MHz, CDCl₃, δ): 7.57 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.23 (dd, *J* = 12.9, 5.0 HZ, 4H),

7.04 (dd, J = 12.5, 6.8 Hz, 8H), 7.01-6.95 (m, 2H), 2.74-2.70 (m, 2H), 2.62-2.59 (m, 2H), 1.99-1.92 (m, 2H). ¹³C NMR (100 MHz, CDCl₃, δ): 148.04, 147.97, 145.84, 136.21, 132.21, 129.19, 124.59, 123.88, 122.49, 119.14, 109.74, 35.64, 34.73, 32.48. MALDI-TOF-MS: 388.33. Anal. calcd for C₂₈H₂₄N₂ (%): C 86.56, H 6.23, N 7.21; found: C 86.28, H 6.45, N 7.19.

Device Fabrication and Measurement

The fabricated devices were grown on clean glass substrates pre-coated with a 180nm thick layer of indium tin oxide (ITO) with a sheet resistance of 15–20 Ω /sq. The ITO surface was treated with oxygen plasma for 2 min, following a degrease in an ultrasonic solvent bath, and then was dried at 120 °C before it was loaded into an evaporator. All layers were grown in succession by thermal evaporation at a pressure below 5 × 10⁻⁴ Pa without breaking vacuum. The thickness of each layer was determined by a quartz thickness monitor. Current–brightness–voltage characteristics were measured using Keithley source measurement units (Keithley 2400 and Keithley 2000) with a calibrated silicon photodiode. The EL spectra were measured using a SpectraScan PR650 spectrophotometer. External quantum efficiencies were calculated from the luminance, current density, and EL spectrum, assuming a Lambertian distribution. All the measurements except the lifetime testing were carried out in an ambient atmosphere. The lifetime measurements were carried out in a nitrogen atmosphere glove box.

Supplemental Table and Figures

guest –	host	
	TPA-BN	TPA-L-BN
FIr6	_	0.41
FIrpic	_	0.53
DMAC-DPS	_	0.60
Ir(ppy) ₂ (acac)	0.66	0.63
PO-01	0.80	0.76
Ir(MDQ) ₂ (acac)	0.85	0.80

Table S1 Absolute fluorescence quantum yields of doped films.



Fig. S1 Fluorescence spectra of (a) TPA-BN films doped with 10 wt% Ir(ppy)₂(acac) and 10 wt% Ir(MDQ)₂(acac), and (b) TPA-L-BN films doped with 10 wt% FIrpic, 10 wt% Ir(ppy)₂(acac) and 10 wt% Ir(MDQ)₂(acac).



Fig. S2 Calculated spatial distributions of the HOMO and LUMO levels.



Fig. S3 (a) Current density-voltage-luminance (J-V-L) characteristics, (b) power efficiency and EQE as a function of luminance, and normalized EL spectra (inset) of the green, orange, and red PhOLEDs based on TPA-L-BN.



7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 fl (ppm)







∼147.54 ∼146.23 √144.00 1146.23 1146.23 114.00 1125.89 125.99 125.89 125.99 12

> 35.64 34.73 32.48





Mass spectroscopy



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