Supplementary Information

Suppressing Triplet State Extension for Highly Efficient Ambipolar Phosphine

Oxide Host Materials in Blue PHOLEDs

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Experimental section

Materials and Instruments

All the reagents and solvents used for the synthesis of the compounds were purchased from Aldrich and Acros companies and used without further purification.

1H NMR spectra were recorded using a Varian Mercury plus 400NB spectrometer relative to tetramethylsilane (TMS) as internal standard. Molecular masses were determined by a FINNIGAN LCQ Electro-Spraying Ionization-Mass Spectrometry (ESI-MS), or a MALDI-TOF-MS. Elemental analyses were performed on a Vario EL III elemental analyzer. Absorption and photoluminescence (PL) emission spectra of using a SHIMADZU the target compound were measured UV-3150 spectrophotometer and a SHIMADZU RF-5301PC spectrophotometer, respectively. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on Shimadzu DSC-60A and DTG-60A thermal analyzers under nitrogen atmosphere at a heating rate of 10 °C min-1. Cyclic voltammetric (CV) studies were conducted using an Eco Chemie B. V. AUTOLAB potentiostat in a typical three-electrode cell with a platinum sheet working electrode, a platinum wire counter electrode, and a silver/silver nitrate (Ag/Ag+) reference electrode. All electrochemical experiments were carried out under a nitrogen atmosphere at room temperature in dichloromethane. Phosphorescence spectra were measured in dichloromethane using an Edinburgh FPLS 920 fluorescence spectrophotometer at 77 K cooling by liquid nitrogen with a delay of 300 µs using Time-Correlated Single Photon Counting (TCSPC) method with a microsecond pulsed Xenon light source for 10 µs-10 s lifetime measurement, the synchronization photomultiplier for signal collection and the Multi-Channel Scaling Mode of the PCS900 fast counter PC plug-in card for data processing.

General procedure of Suzuki coupling

In Ar₂, 6 equivalents of aq. NaOH (2 M) was added to a stirred solution of 1 equivalent of the bromide, 1.5 equivalents of 9-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-9H-carbazole, 0.1 equivalent of Pd(PPh₃)₄ and 0.1 equivalent of TBAB in 10 mL of THF. Then the reaction mixture was heated to 90 °C and stirred for 24 h. The reaction was quenched by 10 mL of aq. NH₄Cl, and extracted by dichloromethane (3×10 mL). The organic layer was dried with anhydride Na₂SO₄. The solvent was removed in vacuo, and then the residue was purified by flash column chromatography.



9-(4'-(2-(diphenylphosphoryl)phenoxy)biphenyl-4-yl)-9H-carbazole

(**DPESPOPhCz**): white powder with the yield of 44%. ¹H NMR (TMS, CDCl₃, 400 MHz): ppm δ = 8.184 (d, *J* = 7.6 Hz, 2H); 8.121 (qd, *J* = 7.6 Hz, 12.8 Hz, 1.6 Hz, 1H); 7.846 (q, *J* = 7.0 Hz, 12.6 Hz, 4H); 7.740 (d, *J* = 8.4 Hz, 2H); 7.633 (d, *J* = 8.4 Hz, 2H); 7.580-7.406 (m, 13H); 7.369-7.266 (m, 3H); 6.897 (q, *J* = 5.2 Hz, 8.0 Hz, 1H); 6.754 (d, *J* = 8.4 Hz, 2H); ¹³C NMR (CDCl₃, 100 MHz): ppm δ = 158.653, 158.623, 154.688, 140.781, 139.272, 136.798, 136.253, 135.177, 135.114, 134.350, 132.279, 132.025, 131.922, 131.615, 131.588, 128.259, 128.181, 128.137, 127.313, 125.951, 123.415, 123.253, 123.206, 123.096, 120.322, 120.007, 117.012, 116.951, 109.748; LDI-TOF: m/z (%): 611 (100) [M⁺]; elemental analysis (%) for C₄₂H₃₀NO₂P: C 82.47, H 4.94, N 2.29, O 5.23; found: C 82.51, H 4.96, N 2.36, O 5.40.

9-(4'-(4'-(9H-carbazol-9-yl)-3-(diphenylphosphoryl)biphenyl-4-yloxy)biphenyl-4-yl)-9H-carbazole (**DPESPOPhCz2**): white powder with the yield of 20%. ¹H NMR (TMS, CDCl₃, 400 MHz): ppm δ = 8.563 (dd, J = 2.0 Hz, 13.2 Hz, 1H); 8.188 (d, J = 7.6 Hz, 4H); 7.996-7.830 (m, 7H); 7.771 (d, J = 8.4 Hz, 2H); 7.721-7.640 (m, 4H); 7.565 (t, J = 7.8 Hz, 4H); 7.531-7.431 (m, 12H); 7.341 (t, J = 7.2 Hz, 4H); 7.022 (q, J = 5.2 Hz, 8.4 Hz, 1H); 6.812 (d, J = 8.4 Hz, 2H); ¹³C NMR (CDCl₃, 100 MHz): ppm δ = 158.137, 158.102, 154.625, 140.827, 139.254, 138.550, 137.126, 136.958, 136.576, 135.544, 133.741, 13.677, 133.234, 132.437, 132.145, 132.039, 131.816, 131.789, 128.417, 128.377, 128.253, 127.416, 126.016, 123.885, 123.479, 122.886, 120.383, 120.342, 120.106, 120.061, 117.520, 117.454, 109.811, 109.768; LDI-TOF: m/z (%): 852 (100) [M⁺]; elemental analysis (%) for C₆₀H₄₁N₂O₂P: C 84.49, H 4.84, N 3.28, O 3.75; found: C 84.53, H 4.81, N 3.40, O 3.92.

9-(4'-(4'-(9H-carbazol-9-yl)-3-(diphenylphosphoryl)biphenyl-4-yloxy)-3'-(9H-carb azol-9-yl)phenyl-biphenyl-4-yl)-9H-carbazole (**DPESPOPhCz3**): white powder with the yield of 40%. ¹H NMR (TMS, CDCl₃, 400 MHz): ppm δ = 8.550 (dd, *J* = 2.0 Hz, 13.2 Hz, 1H); 8.264-8.163 (m, 6H); 7.954-7.837 (m, 8H); 7.808 (d, *J* = 2.0 Hz, 1H); 7.670 (q, *J* = 8.4 Hz, 12.0 Hz, 4H); 7.568 (q, *J* = 8.6 Hz, 16.6 Hz, 4H); 7.550-7.302 (m, 26H); 7.075 (q, *J* = 5.2 Hz, 8.4 Hz, 1H); 6.611 (d, *J* = 8.4 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz): ppm δ = 158.176, 158.414, 152.348, 140.762, 140.633, 138.970, 138.333, 137.145, 137.093, 136.871, 136.153, 135.766, 135.660, 133.553, 133.493, 133.117, 132.537, 132.116, 132.014, 131.865, 130.492, 129.678. 128.409, 128.372, 128.307, 127.596, 127.414, 127.378, 126.701, 125.990, 123.516, 123.467, 120.482, 120.411, 120.316, 120.172, 120.080, 120.035, 118.809, 110.746, 109.803, 109.761, 109.725; LDI-TOF: m/z (%): 1093 (100) [M⁺]; elemental analysis (%) for C₇₈H₅₂N₃O₂P: C 85.62, H 4.79, N 3.84, O 2.92; found: C 85.64, H 4.77, N 3.95, O 3.07.

9-(3'-(diphenylphosphoryl)-4'-(2-(diphenylphosphoryl)phenoxy)biphenyl-4-yl)-9Hcarbazole (**DPEPOPhCz**): white powder with the yield of 60%. ¹H NMR (TMS, CDCl₃, 400 MHz): ppm δ = 8.221 (d, *J* = 13.2 Hz , 1H); 8.159 (d, *J* = 7.6 Hz, 2H); 7.894-7.653 (m, 10H); 7.649-7.493 (m, 6H); 7.497-7.220 (m, 16H); 7.192 (d, *J* = 7.6 Hz, 1H); 7.090 (t, *J* = 7.2 Hz, 1H); 6.282 (t, *J* = 5.6 Hz, 1H); 6.063 (t, *J* = 4.8 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz): ppm δ = 158.653, 158.623, 140.781, 139.272, 136.798, 136.253, 135.177, 135.114, 134.044, 133.350, 132.279, 132.025, 131.922, 131.615, 131.588, 128.259, 128.181, 128.137, 127.313, 125.951, 123.415, 123.253, 123.206, 123.096, 122.240, 120.322, 120.007, 117.012, 109.748; LDI-TOF: m/z (%): 811 (100) [M^+]; elemental analysis (%) for C₅₄H₃₉NO₃P₂: C 79.89, H 4.84, N 1.73, O 5.91; found: C 79.95, H 4.89, N 1.94, O 6.08.

9,9'-(4',4''-oxybis(3'-(diphenylphosphoryl)biphenyl-4',4-diyl))bis(9H-carbazole) (**DPEPOPhCz2**): white powder with the yield of 55%. ¹H NMR (TMS, CDCl₃, 400 MHz): ppm δ = 8.171 (d, *J* = 7.6 Hz 4H); 8.118 (d, *J* = 13.2 Hz, 2H); 7.901-7.685 (m, 12H); 7.675-7.606 (m, 4H); 7.600-7.293 (m, 26H); 6.272 (s, 2H); ¹³C NMR (CDCl₃, 100 MHz): ppm δ = 158.331, 140.699, 138.131, 137.230, 136.100, 135.993, 132.582, 132.511, 132.206, 132.043, 131.937, 131.679, 128.598, 128.477, 128.272, 128.169, 127.350, 125.986, 125.219, 124.228, 123.448, 120.801, 120.737, 120.329, 120.070, 109.712; LDI-TOF: m/z (%): 1052 (100) [M⁺]; elemental analysis (%) for C₇₂H₅₀N₂O₃P₂: C 82.11, H 4.79, N 2.66, O 4.56; found: C 82.17, H 4.75, N 2.83, O 4.71.

DFT Calculations

The DFT computations were carried out with different parameters for structure optimizations and vibration analyses. The ground states and triplet states of molecules in vacuum were optimized without any assistance of experimental data by the restricted and unrestricted formalism of Beck's three-parameter hybrid exchange functional¹ and Lee, and Yang and Parr correlation functional² (B3LYP)/ 6-31G(d) respectively. The fully optimized stationary points were further characterized by harmonic vibrational frequency analysis to ensure that real local minima had been found without imaginary vibrational frequency. The total energies were also corrected by zero-point energy both for the ground state and triplet state. The Spin Density Distributions were visualized with Gaussview 3.0. All computations were performed using the Gaussian 03 package.³

Device Fabrication and Testing

The OLEDs with configurations of ITO|MoO₃ (10nm)|NPB (70nm)|TCTA (5nm)|**DPExPOPhCzn**:FIrpic (15%, 20nm)|TPBi (35nm)|LiF (1nm)|Al were

fabricated, where MoO_3 and LiF served as hole- and electron-injecting layers, NPB is N,N-bis(naphthylphenyl)-4,4'-biphenyldiamine as the hole-transporting layer 1,3,5-tris(1-phenyl-1H-benzo[d]imidazol-2-yl)benzene (HTL), TPBI is as hole-blocking TCTA electron-transporting layer, and is tris(4-(9H-carbazol-9-yl)phenyl)amine as exciton-blocking layer, respectively. The hole-only and electron-only devices were fabricated with the structures of ITO|MoO_x (10 nm)|NPB (70 nm)|TCTA (5 nm)|Host (20 nm)|TCTA (5 nm)|NPB (70 nm)|MoO₃ (10 nm)|Al and ITO|LiF (1 nm)|TPBI (35 nm)|Host (20nm)|TPBI (35 nm)|LiF (1 nm)|Al, respectively. Before loading into a deposition chamber, the ITO substrate was cleaned with detergents and deionized water, dried in an oven at 120 °C for 4 h, and treated with UV-ozone for 20 min. Devices were fabricated by evaporating organic layers at a rate of 0.1-0.3 nm s⁻¹ onto the ITO substrate sequentially at a pressure below 1×10^{-6} mbar. Onto the TPBI layer, a layer of LiF with 0.5 nm thickness was deposited at a rate of 0.1 nm s⁻¹ to improve electron injection. Finally, a 100-nm-thick layer of Al was deposited at a rate of 0.6 nm s⁻¹ as the cathode. The emission area of the devices was 0.14 cm^2 as determined by the overlap area of the anode and the cathode. The EL spectra and CIE coordinates were measured using a PR650 spectra colorimeter. The current-density-voltage and brightness-voltage curves of the devices were measured using a Keithley 2400/2000 source meter and a calibrated silicon photodiode. All the experiments and measurements were carried out at room temperature under ambient conditions.

Single Crystal Structure of DPEPOPhCz



Figure S1. Single crystal structure (above) and the packing diagram (below) of **DPEPOPhCz**. The suitable crystal was obtained through slow evaporation of its ethanol solution.



Thermal Properties of DPExPOPhCzn

Figure S2. TGA and DSC (inset) curves of DPExPOPhCzn.

Optical Properties of DPExPOPhCzn Dispersed in PS and PMMA Films



Figure S3. Absorption and PL spectra of **DPExPOPhCzn** dissolved in PS (above) and PMMA (below) matrixes (8%).



DFT Calculation Results

Figure S4. Contours and energy levels of the FMOs of DPExPOPhCzn.

Electrochemical Properties of DPExPOPhCzn



Figure S5. CV curves of **DPExPOPhCzn** measured at room temperature with the scanning rate of 100 mV s⁻¹.



Carrier Transporting Properties of DPExPOPhCzn

Figure S6. IV characteristics of single-carrier transporting devices based on **DPExPOPhCzn**.

Energy Level Scheme of the PHOLEDs



Scheme S1. Energy level scheme of **PA-PE** and the chemical structures of the involved materials.

Efficiency vs. Current Density of the Blue PHOLEDs based on DPExPOPhCzn



Figure S7. Efficiency-*J* curves of PA-PE.





Figure S8. Time decay curves of FIrpic-originated emission at 475 nm from FIrpic-doped **DPExPOPhCzn** films (8%) with excitation at 300 nm.

Compound	Absorption (nm)	Emission (nm)	PLQY ^[c] (%)	S ₁ (eV)	T ₁ (eV)	$\binom{T_{\rm g}/T_{\rm m}}{C}$	HOMO (eV)	LUMO (eV)
DPESPOP hCz	331, 309, 293,263, 227 ^[a] 345, 319, 297,258, 231 ^[b]	352, 369, 389 ^[a] 373, 405, 430 ^[b]	52	3.58 [d] 4.23 [e]	3.00 [[] 3.17 [[] e]	-/192/44 8	-6.16(1.3 8) ^[g] /-5.3 7 ^[e]	-2.49(-2. 29) ^[g] /-1. 14 ^[e]
DPESPOP hCz2	342, 315, 293,260, 235 ^[a] 341, 314, 294,255, 235 ^[b]	352, 385 ^[a] 381, 405, 425 ^[b]	94	3.51 [d] 4.02 [e]	3.00 [[] 3.17 [[]	230/-/50 5	-6.13(1.3 5) ^[g] /-5.2 8 ^[e]	-2.52(-2. 26) ^[g] /-1. 26 ^[e]
DPESPOP hCz3	340, 310, 293,265, 239 ^[a] 343, 330, 296,266, 236 ^[b]	350, 385 ^[a] 385, 405, 425 ^[b]	73	3.51 ^[d] 3.94 ^[e]	2.84 [[] 2.82 [[] e]	222/-/51 4	-6.13(1.3 5) ^[g] /-5.3 0 ^[e]	-2.55(-2. 23) ^[g] /-1. 36 ^[e]
DPEPOPh Cz	344, 315, 295,262, 229 ^[a] 346, 324, 298,266, 232 ^{b]}	396 ^[a] 385, 404, 425 ^[b]	81	3.52 ^[d] 4.21 ^[e]	2.91 [[] 3.14 [[] e]	239/272/ 452	-6.19(1.4 1) ^[g] /-5.2 8 ^[e]	-2.62(-2. 16) ^[g] /-1. 06 ^[e]
DPEPOPh Cz2	343, 310, 295,265, 239 ^[a] 347, 329, 298,264, 235 ^{b]}	389 ^[a] 384, 405, 428 ^[b]	79	3.47 ^[d] 4.13 ^[e]	2.83 [[] 2.82 [[] e]	231/-/46 7	-6.16(1.3 8) ^[g] /-5.3 0 ^[e]	-2.64(-2. 14) ^[g] /-1. 17 ^[e]

Table S1. Physical properties of the PO hosts.

[a] in CH_2Cl_2 (10⁻⁶ mol L⁻¹); [b] in film; [c] calculated by using 9,10-diphenylanthracene as standard; [d] estimated according to the absorption edges; [e] DFT calculated results; [f] calculated according to the 0-0 transitions of the phosphorescence spectra; [g] calculated according to the equation HOMO/LUMO = 4.78 + onset voltage.

Table S2. EL performance of the hosts for PHOLEDs.

Device	Operating Voltage	Maximum Efficiencies ^b	Efficiency Roll-Offs (%) ^c		
	$(V)^{a}$		C.E.	P.E.	E.Q.E.
PA	3.1, <4.1, <5.7	32.0, 25.1, 13.6	-, 11	3, 37	-, 11
PB	3.1, <4.3, <6.5	27.4, 27.7, 11.6	23, 40	44, 71	22, 40
PC	3.3, <4.7, <6.7	24.5, 23.3, 10.1	23, 34	48, 68	23, 36
PD	3.1, <4.9, <7.3	10.0, 9.5, 4.2	11, 25	40, 66	10, 24
PE	3.3, <6.7, <10.7	2.8, 2.5, 1.2	50, 68	72, 88	50, 67

^a In the order of onset, 100 and 1000 cd m⁻²; ^b in the order of C.E. (cd A^{-1}), P.E. (lm W^{-1}) and E.Q.E. (%); c in the order of 100 and 1000 cd m⁻².

References

- 1. A. D. Becke, J. Chem. Phys., 1993, 98, 5648-5652.
- 2. C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785-789.
- 3. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, T. V. Jr., K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Octhterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, A. L. G. Liu, P. Piskorz, I. Komaromi, R. L.Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, Gaussian 03, Revision D.02, Gaussian Inc., Pittsburgh, PA, 2004.