Electronic Supplementary Information (ESI)

Host material consisting of phosphinic amide directly linked donor-acceptor structure for efficient blue phosphorescent organic light-emitting diodes

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Experimental section:

General. ¹H and ¹³C NMR spectra were recorded on an Avance III 500 spectrometer (Bruker Biospin). Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were obtained on an Autoflex III spectrometer (Bruker Daltonics) in reflection/positive mode with a dithranol matrix. Elemental analysis was performed using an MT-5 CHN analyzer (Yanaco). Solvents and reagents were purchased from Sigma-Aldrich, Tokyo Chemical Industry, or Wako Chemicals, and were used without further purification. *N*-(4-diphenylphosphoryl)carbazole (**2**) and *N*-(4-diphenylphosphorylphenyl)carbazole (**3**) were synthesized according to the procedures in the literature.^{S1} TAPC, mCP, and FIr6 were purchased from Luminescence Technology Corporation and were used as received.

Synthesis of 3,6-di-tert-butyl-N-(4-diphenylphosphoryl)carbazole (1). To a stirred solution of 3,6-di-tert-butylcarbazole (0.97 g, 3.48 mmol) in dry diethyl ether (15 mL) was added dropwise n-butyllithium (1.6 M, 3.2 mL, 5.2 mmol) at -78 °C. The mixture was allowed to react for 1 h at that temperature. Diphenylphosphine chloride (0.77 g, 3.48 mmol) was added dropwise at -78 °C, and the mixture was stirred first at -78 °C for 1 h, and then at room temperature overnight. The product was purified by column chromatography on silica using dichloromethane as an eluent. The phosphine compound obtained was dissolved in chloroform and ethanol, and was then oxidized by treatment with an aqueous hydrogen peroxide (30%, 1.0 mL) for 4 h to form 1 as a white powder. Compound 1 was further purified by temperature-gradient sublimation under a vacuum (yield = 1.25 g, 75%). ¹H NMR (CDCl₃, 500 MHz): δ 8.00 (s, 2H), 7.76-7.72 (m, 4H), 7.63-7.60 (t, J = 7.5 Hz, 2H), 7.50-7.46 (t, J = 7.7 Hz, 4H), 7.23-7.21 (d, J = 8.8 Hz, 2H), 7.15-7.13 (d, J = 8.8 Hz, 2H), 1.39 (s, 18H). ¹³C NMR (CDCl₃, 125 MHz): δ 144.8, 140.0, 133.0, 132.2, 132.1, 131.7, 130.7, 129.0, 128.9, 126.5, 126.4, 124.0, 115.8, 114.3, 34.6, 31.8. MALDI-TOF-MS: m/z 480.16 ($[M+H]^+$). Anal. Calcd for C₃₂H₃₄NOP: C, 80.14; H, 7.15; N, 2.92%. Found: C, 80.01; H, 7.10; N, 2.86%.

X-ray crystallography. X-ray structural analysis was performed at the Analytical Center of the Institute for Materials Chemistry and Engineering, Kyushu University. All the data were collected at 123 K on a Rigaku R-AXIS RAPID diffractometer using graphite monochromated Cu-K α radiation ($\lambda = 1.54187$ Å). Data reductions of the measured reflections were carried out using the CrystalStructure (ver. 4.0) software package. The structure was solved by direct methods and was refined by a full-matrix least-squares technique based on all F^2 data using SHELX97.^{S2} CCDC-894700 for **1**

contains the supplementary crystallographic data for this paper.

DFT calculations. The density-functional theory (DFT) calculations were performed using Gaussian 03 at the B3LYP level.^{S3} The ground state geometry was inferred from the crystal structure, and the molecular orbitals were calculated using 6-31G(d) as a basis set for C, H, N, O and P atoms.

Thermal measurements. Thermogravimetric analysis (TGA) was performed on a Bruker TAPS3000S under a nitrogen atmosphere at a heating rate of 10 °C/min. Differential scanning calorimetry (DSC) was performed using a Netzsch DSC 204 F1 at a heating rate of 5 °C /min.

Photophysical measurements. Absorption spectra were measured in tetrahydrofuran and in thin films at room temperature with a Lambda 950-PKA absorption spectrometer (PerkinElmer). Photoluminescence (PL) spectra were measured in tetrahydrofuran and in thin films at room temperature with an FP-6500-ST photoluminescence spectrometer (JASCO). Phosphorescence spectra were measured in 2-methyltetrahydrofuran and in thin films at 77 K with a delay of 10 ms after the excitation pulse using an FP-6500-A-51 photoluminescence spectrometer (JASCO). The PL lifetimes were measured using a streak camera system (Hamamatsu, C4334) with a N₂ gas laser (MNL200, Laser Technik Berlin, $\lambda = 337$ nm) as an excitation source. PL quantum efficiencies were measured with an absolute photoluminescence quantum yield measurement system (Hamamatsu, C9920-02). The highest occupied molecular orbital (HOMO) levels of all materials were estimated from their ionization potential energies (Ip) in thin films. Ip values were determined by ultraviolet photoelectron spectroscopy in air (AC-3, Riken-Keiki). The lowest unoccupied molecular orbital (LUMO) levels were estimated by subtracting the optical energy gaps (E_g) from the HOMO energies. The E_{g} values were determined from the absorption onset energies.

OLED fabrication and measurements. The organic and metal layers were deposited by thermal evaporation in a vacuum chamber with a base pressure of $<3.5\times10^{-4}$ Pa. TAPC with a thickness of ~40 nm, mCP with a thickness of ~10 nm, the emitting layer (device A, 1:10 wt.% FIr6; device B, 3:10 wt.% FIr6) with a thickness of ~20 nm, and DPEPO with a thickness of ~40 nm were deposited successively. Finally, cathodes composed of LiF with a thickness of ~0.7 nm and Al with a thickness of ~100 nm were deposited on the organic layers. The current density–voltage–luminance characteristics of the OLEDs were measured at ambient temperature using a semiconductor parameter analyzer (Agilent, E5273A) and an optical power meter (Newport, 1930C). The

electroluminescence (EL) spectra of the devices were obtained using a multichannel spectrometer (Ocean Optics, USB2000).

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Figure S1. TGA curves of compounds 1, 2, and 3.



Figure S2. DSC curves of compounds 1, 2, and 3.



Figure S3. Optical microscopic images of compounds **1** (left), **2** (center), and **3** (right). The thin films were prepared by thermal evaporation on Si substrates.



Figure S4. Transient PL decay for 10 wt.% FIr6-doped 1 (left) and 3 (right) films.



Figure S5. Current efficiency–current density (left) and power efficiency–current density plots (right) for Devices A and B.