

Electronic Supporting Information

Phosphorescent OLEDs Assembled Using Os(II) Phosphors and Bipolar Host Material Consisting of Both Carbazole and Dibenzophosphole Oxide

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Experimental Section

General procedures: All reactions were performed under argon atmosphere and solvents were distilled from appropriate drying agents prior to use. Commercially available reagents were used without further purification unless otherwise stated. All reactions were monitored using pre-coated TLC plates (0.20 mm with fluorescent indicator UV254). Differential scanning calorimetry (DSC) was characterized with a TA DSC Q200 at a heating rate of 10 °C min⁻¹ from 20 to 250 °C under nitrogen. The glass transition temperature (*T_g*) was determined from the second heating scan. Thermogravimetric analysis (TGA) was measured with a Perkin-Elmer Pyris 1 TGA instrument. Mass spectra were obtained on a JEOL SX-102A instrument operating in electron impact (EI) or fast atom bombardment (FAB) mode. ¹H NMR spectra were recorded on a Varian Mercury-400 or an INOVA-500 instrument. Elemental analysis

was carried out with a Heraeus CHN-O Rapid Elementary Analyzer.

Synthesis of 9-(4-bromophenyl)carbazole: Carbazole (8.35 g, 50 mmol), 1-bromo-4-iodobenzene (16.97 g, 60 mmol), CuI (0.95 g, 5 mmol), 1,10-phenanthroline (1.80 g, 10 mmol) and K₂CO₃ (14.49 g, 105 mmol) were suspended in DMF (500 mL). The mixture was heated to 120 °C for 24 hr. After cooling to room temperature, the solvent was removed under vacuum and the residue was extracted with CH₂Cl₂ (50 mL × 3) and dried over MgSO₄. The solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica gel eluting with hexane to give white solid (12.07 g, 37.48 mmol, 75%).

Spectral data of **9-(4-bromophenyl)carbazole**: MS (EI) : m/z 321 (M)⁺; ¹H NMR (400 MHz, CDCl₃, δ): 8.12 (d, J = 7.6 Hz, 2H), 7.71 (d, J = 8.8 Hz, 2H), 7.44 (d, J = 8.4 Hz, 2H), 7.40 ~ 7.35 (m, 4H), 7.26 ~ 7.3 (t, J = 6.8 Hz, 2H).

Synthesis of 5-phenyldibenzophosphole: To a solution of triphenylphosphine oxide (14.0 g, 50.0 mmol) in THF (400 mL) at 0 °C under N₂ atmosphere was added 2 M phenyllithium (52.5 mL, 105 mmol). After refluxed for 12 h, the solvent was removed under vacuum. To the residue was added water (200 mL) and the mixture was neutralized with 1 M hydrochloric acid, extracted with dichloromethane. The extract was dried with MgSO₄ and the solvent was evaporated under reduced pressure. The crude was purified by column chromatography over silica gel eluting with hexane to give 5-phenyldibenzophosphole (7.91 g, 30.42 mmol, 61%).¹

Spectral data of **5-phenyldibenzophosphole**: MS (EI) : m/z 260 (M)⁺; ¹H NMR (400 MHz, CDCl₃, δ): 7.93 (d, J = 7.9 Hz, 2H), 7.67 ~ 7.71 (m, 2H), 7.45 (t, J = 7.9 Hz, 2H), 7.26 ~ 7.34 (m, 4H), 7.18 ~ 7.25 (m, 3H).

Synthesis of 5-*H*-dibenzophosphole: 5-Phenyldibenzophosphole (6.7 g, 25.7

mmol) and granular lithium (0.5 g, 71 mmol) were placed in a 50 mL flask and THF (25 mL) was added under nitrogen. After stirring for 6 h, the dark mixture was cannulated to another 50 mL flask. This dark mixture was added degassed water (5.16 mL) followed by degassed acetic acid (15.5 mL) to give a yellowish suspension. The mixture was dried under vacuum and the residual was filtered by aluminum oxide using DCM. After removal of all volatiles, the residual solid was dissolved in dry pentane and filtered over glass wool. After evaporation to dryness in vacuum, **5-*H*-dibenzophosphole** was obtained as a white solid (3.64 g, 19.78 mmol, 76%).

Spectral data of **5-*H*-dibenzophosphole**: ^1H NMR (400 MHz, CDCl_3 , δ): 7.96 (d, $J = 8$ Hz, 2H), 7.84 ~ 7.81 (m, 2H), 7.48 (t, $J = 8$ Hz, 2H), 7.38 ~ 7.35 (m, 2H), 5.29 (d, $^1J(\text{H,P}) = 200$ Hz, 1H).

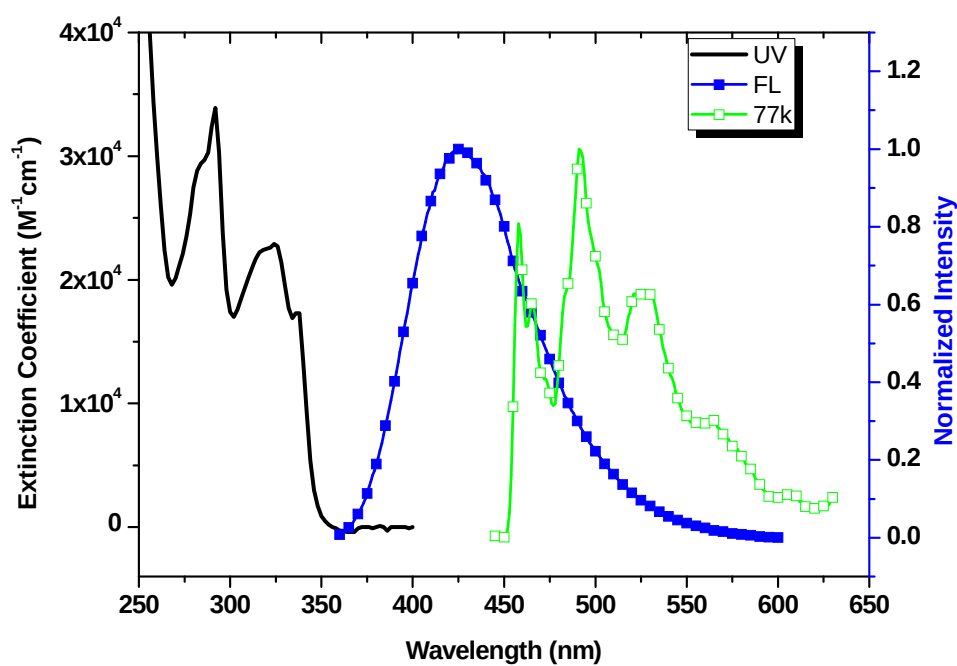


Figure S1. Absorption and emission spectra of **CzPhO**: absorbance, fluorescence (RT) spectra in degassed CH_2Cl_2 , and phosphorescence spectra (77K) in 2-Methyltetrahydrofuran.

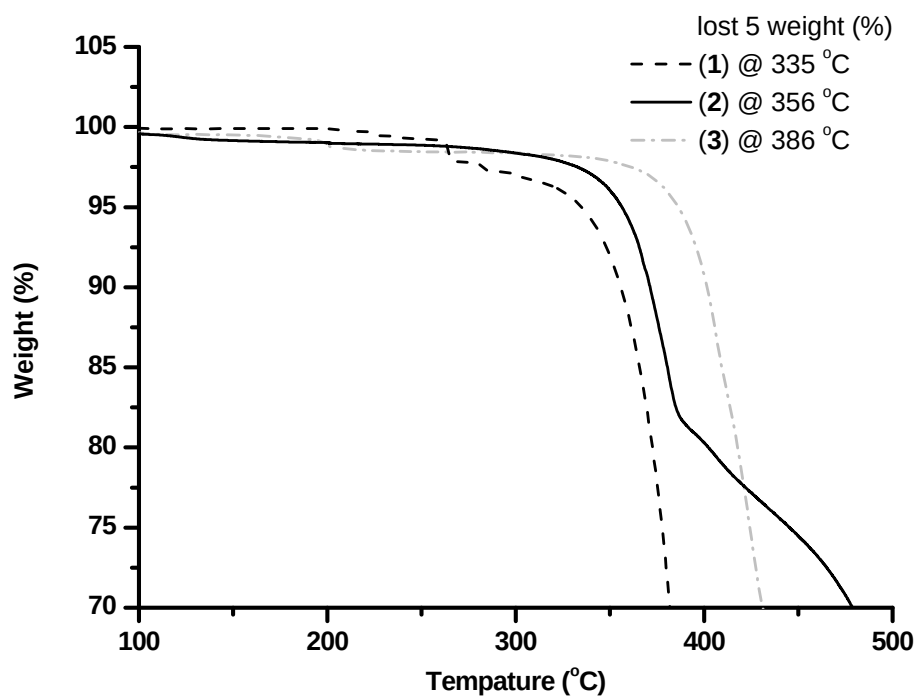


Figure S2. TGA data for complexes **1** ~ **3**. Thermogravimetric (TGA) data were performed on Perkin Elmer Pyris Diamond TG-DTA under nitrogen, for which the heating rate was 5 °C/min.

¹ S. Ogawa, Y. Tajiri and N. Furukawa, *Bull. Chem. Soc. Jpn.*, 1991, **64**, 3182.