Experimental Section

General Procedures

^{1}H NMR and ^{13}C NMR spectra were measured with a Varian Gemini-400 Varian spectrometer. Mass spectra were recorded on a Finnigan 4021C GC-MS spectrometer. The absorption and photoluminescence spectra were recorded on a Hitachi U-3010 UV−vis spectrophotometer and a Hitachi F-4600 fluorescence spectrophotometer, respectively. The phosphorescence spectrum was measured in 2-MeTHF glass matrix at 77 K using a Hitachi F-4600 fluorescence spectrometer. Cyclic voltammetry was performed on a CHI660E electrochemical analyzer. The electrolytic cell was a conventional three-electrode cell in which a glassy carbon working electrode, a platinum wire auxiliary electrode, and an aqueous saturated calomel electrode (SCE) as the reference electrode were employed. The ferrocene/ferrocenium couple was used as the internal standard. Tetra-n-butylammoniumhexafluorophosphate ($TBAPF_6$, 0.10 M) was used as the supporting electrolyte and DMF as the solvent, respectively.

Synthesis

Commercially available reagents and materials were used without further purification. The synthetic route of SOTPA is outlined in Scheme 1.

4-bromo-diphenylsulfide. Diphenylsulfide (3.34 mL, 20 mmol) was dissolved in a mixed solution of CH_2Cl_2 and H_2O (1:1, 150 mL). Then 30% hydrogen peroxide (0.86 mL, 36 mmol) and bromine (1 mL, 20 mmol) were added, and the reaction solution was continuously stirred for 6 h. The resulting mixture was extracted with CH_2Cl_2 with surplus bromine removed by saturated Na_2SO_3 solution. After removing the CH_2Cl_2 solvent, the residue was further purified by silica gel column chromatography (petroleum ether) to give 4.57 g (86%) a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.44 (s, 2H), 7.42 (s, 2H), 7.19 (dd, J = 8.2, 2.7 Hz, 5H). EI MS (m/z): 265.94.

4-bromo-diphenylsulfone. 4-bromo-diphenylsulfide (2.66g, 10mmol), $KMnO_4$ (8.0 g, 50.6 mmol), and $MnSO_4$ monohydrater (8.0 g, 47.3 mmol) were stirred continuously in CH_2Cl_2 (75 mL) for 10 h. After that, the reaction mixture was filtered, and the residue was washed with additional CH_2Cl_2. The crude product was obtained by evaporation of the collected CH_2Cl_2 and was further purified via silica gel column chromatography using CH_2Cl_2/petroleum ether (2:1) as the eluent to give 2.45 g (83%) a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.95 – 7.91 (m, 2H), 7.83 – 7.77 (m, 2H), 7.68 – 7.61 (m, 2H), 7.58 (dd, J = 6.0, 3.9 Hz, 1H), 7.55 – 7.48 (m, 2H). EI MS (m/z): 295.95.

4-(4-diphenylaminophenyl)diphenylsulfone (SOTPA). Toluene (22.5 mL), ethanol (7.5 mL), and 2 M aqueous Na_2CO_3 (15 mL) were added to a mixture of 4-bromo-diphenylsulfone (1.48 g, 5 mmol), 4-diphenylaminophenylboronic acid (2.89 g, 10 mmol), and

tetrakis(triphenylphosphine)platinum (585 mg, 0.5 mmol). With stirring, the suspension was heated at 90°C for 24 h under nitrogen atmosphere. When cooled to room temperature, the mixture was extracted with CH_2Cl_2 and dried over Na_2SO_4. After the solvent had been removed, the residue was purified by column chromatography on silica gel using CH_2Cl_2/petroleum ether (3:1) as the eluent to give 1.56 g (73%) a white solid. ^{1}H NMR (400 MHz, DMSO) δ (ppm) 8.01 – 7.93 (m, 4H), 7.84 (d, *J* = 8.7 Hz, 2H), 7.68 (ddd, *J* = 6.3, 3.7, 1.3 Hz, 1H), 7.66 – 7.59 (m, 4H), 7.37 – 7.29 (m, 4H), 7.14 – 7.03 (m, 6H), 6.99 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 147.38, 145.68, 142.14, 139.52, 133.04, 129.72, 129.44, 129.27, 129.16, 128.27, 128.02, 127.66, 127.17, 125.01, 123.61, 123.05. EI MS (m/z): 461.16.

Quantum Calculation

Theoretical calculation of the compound was carried out using the Gaussian-03 program. Density functional theory (DFT) B3LPY/6-31G (d) was used to determine and optimize the structure

Device Fabrication and Measurement

ITO-coated glasses with a sheet resistance of 30 Ω per square were used as substrates. Before device fabrication, the ITO glass substrates were cleaned with isopropyl alcohol and deionized water, dried in an oven at 120 °C, treated with UV-ozone, and finally transferred to a vacuum deposition system with a base pressure better than 1×10^{-6} torr for organic and metal deposition. Thermally evaporated organic materials were sequentially deposited at a rate of 1−2 Å s^{-1} onto the ITO substrates. The cathode was completed by thermal deposition of LiF at a deposition rate of 0.1 Å s^{-1}, and then capped with Al metal deposited at a rate of 10 Å s^{-1}. EL luminescence spectra and CIE color coordinates were measured with a Spectrascan PR650 photometer, and the current-voltage characteristics were measured with a computer-controlled Keithley 2400 SourceMeter under ambient atmosphere. EQE was calculated from the current density, luminance, and EL spectrum, assuming a Lambertian distribution. The emitting area of the device is 0.1 cm^2.

Supporting Information

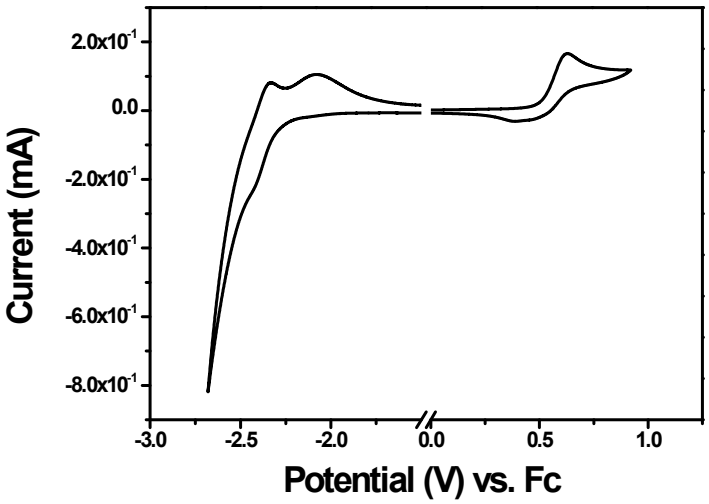

Figure S1. Cyclic voltammograms of SOTPA in DMF with 0.1 M Bu_4NPF_6 as a supporting electrolyte, saturated calomel electrode (SCE) as a reference electrode, Pt disk as a working electrode, and a scan rate of 100 mV s^{-1}. Fc/Fc^+ was used as external reference.

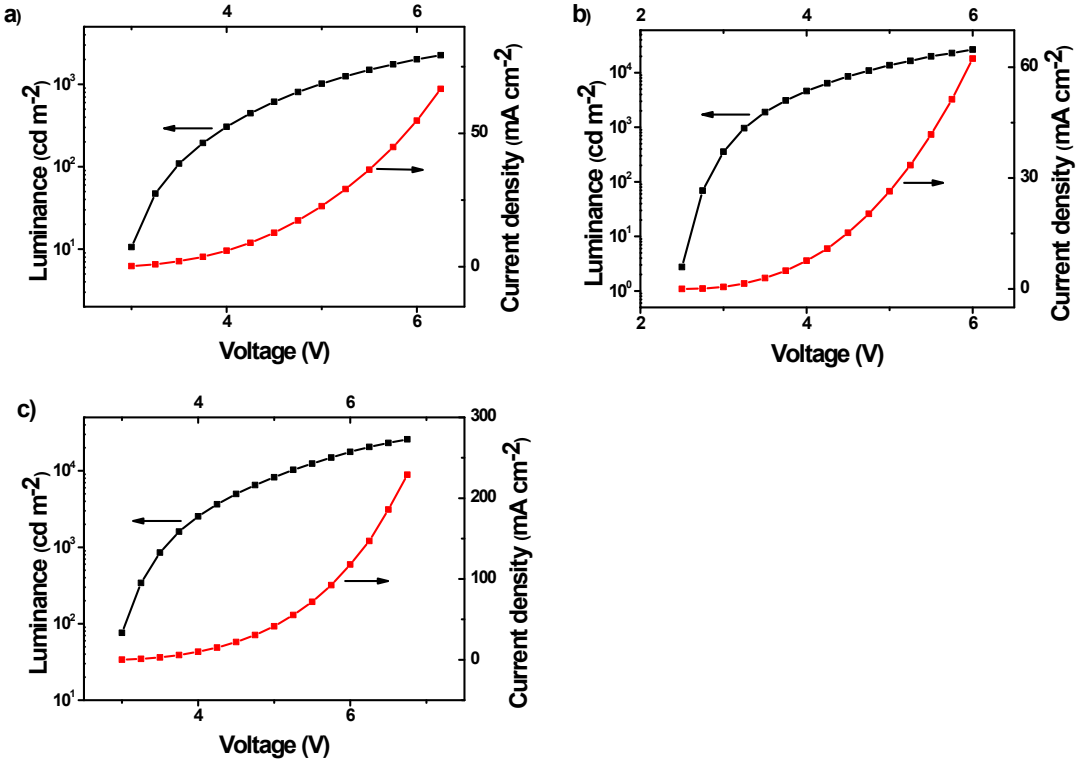

Figure S2. Luminance-voltage-current density characteristics of (a) device B, (b) device G and (c) device R.

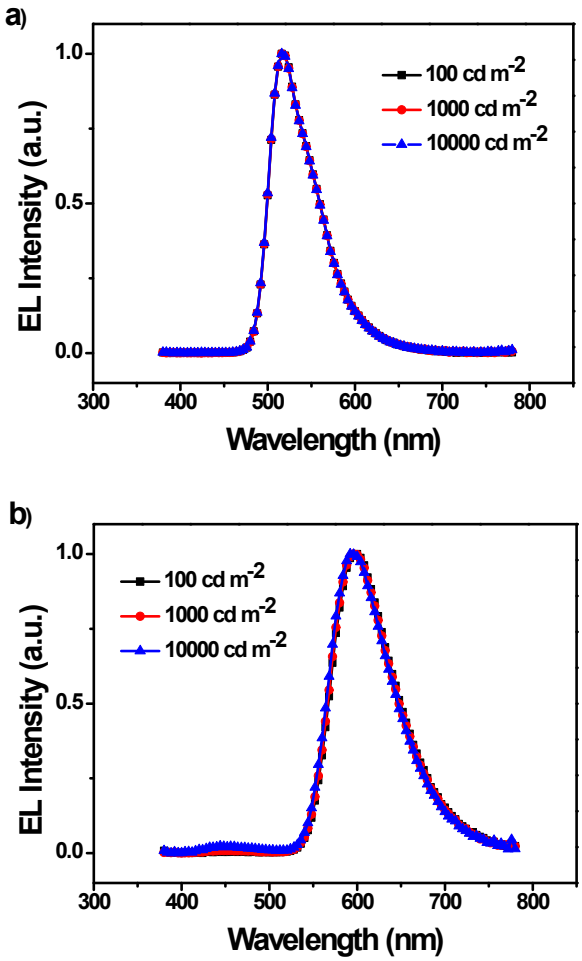

Figure S3. EL spectra of (a) device G and (b) device R.

Table S1. The CIE coordinates of the SOTPA based single-EML F−P hybrid WOLED (device W).

Luminance	100 cd m^{-2}	1000 cd m^{-2}	10000 cd m^{-2}
CIE(x, y)	(0.46, 0.46)	(0.45, 0.44)	(0.39, 0.39)