Electronic Supplementary Information (ESI) for XXXXXXXX

A single-molecule excimer-emitting compound for highly efficient fluorescent organic light-emitting devices

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Experimental Section

1. Measurements and OLEDs Fabrications.

The ^{1}H NMR spectra were recorded on JEOL 400 (400 MHz) spectrometers. Mass spectra were obtained using a JEOL JMS-K9 mass spectrometer. Differential scanning calorimetry (DSC) was performed using a Perkin-Elmer Diamond DSC Pyris instrument under nitrogen atmosphere at a heating rate of 10 ˚C min^{-1}. Thermogravimetric analysis (TGA) was undertaken using a SEIKO EXSTAR 6000 TG/DTA 6200 unit under nitrogen atmosphere at a heating rate of 10 ˚C min^{-1}. Absorption and fluorescence spectra were recorded respectively with a Shimadzu UV-3150 UV-vis-NIR spectrophotometer and a FluroMax-4 (Jobin-Yvon-Spex) luminescence spectrometer. The highest occupied molecular orbital (HOMO) value was measured directly by atmospheric ultraviolet photoelectron spectroscopy (Rikken Keiki AC-3), whereas the lowest unoccupied molecular orbital (LUMO) value was determined from the HOMO and position of the lowest energy absorption edge of the UV absorption spectra.

OLEDs were fabricated by vacuum deposition on ITO glass substrates with a sheet resistance of 30 Ω /square. Before deposition, the ITO substrate was carefully cleaned, treated with UV-ozone then loaded into a deposition chamber. The devices were fabricated by evaporating organic layers onto the ITO substrate sequentially at an evaporation rate of 2-4 Å /s and a pressure better than 5×10^{-6} mbar. Electroluminescence (EL) spectra and CIE color coordinates were taken by an optical multichannel analyzer, Hamamatsu PMA 11, and the current density–luminance–voltage characteristics of the OLEDs were measured with Keithley source meter 2400 and Konica Minolta CS-200, respectively.

2. Materials Synthesis

Pyrene-2-monoboronate ester (1)[1]. Bis(pinacolato)diboron (DOB) (8.90 g, 35.0 mmol), 4,4’-di-*tert*-butyl-2,2’-bipyridine (dtbpy) (1.34 g, 5.0 mmol), and $[Ir(OMe)COD]_2$ (1.60 g, 2.5 mmol) were added to a solution of pyrene (10.11 g, 50.0 mmol) in dry cyclohexane (250 mL). After nitrogen gas had been bubbled into the mixture for 30 min, the mixture was heated to 75 ^{o}C for 12 h under N_2.

The resulting solution was diluted with CH_2Cl_2 (500 mL) and was concentrated to leave an oily residue, which was directly subjected to column chromatography to give the desired mono-borylated product as pale yellow solid. Yield: 1.85 g (46%); ^1H NMR (400 MHz, $CDCl_3$): δ 1.47 (s, 12H), 7.99-8.02 (t, 1H), 8.09 (d, 2H, $J = 4.2$ Hz), 8.09 (d, 4H, $J = 7.8$ Hz), 8.64 (s, 2H) ppm. EI-MS: *m/z* 328 [M^+]. Anal. Calcd for $C_{22}H_{21}BO_2$: C, 80.51; H, 6.45. Found: C, 80.45; H, 6.52.

1, 8-Dibromonaphthalene (2)[2]. To a mixture of the corresponding amine (3.62 g, 22.86 mmol) in HBr (48%, 14.0 mL) cooled to -5 ˚C, was slowly added a cold solution of $NaNO_2$ (3.16 g, 45.72 mmol) in H_2O (6.0 mL). After stirring for 30 min at -5 ˚C, the precipitate formed and was diluted with HBr (100 mL, 48%). The mixture was directly added into a stirred suspension of CuBr (3.61 g, 25.15 mmol) in HBr (48%, 4.0 mL) at 80 ˚C. The mixture was stirred for 30 min at 80 ˚C. After reactions, the mixture was cooled to room temperature, diluted with water and toluene, the precipitate formed was filtered and washed with water and toluene, the filter was collected and extracted with toluene, washed with water and brine. The organic solvents were removed under vacuum, and the residue was subjected to column chromatography (eluent: hexane) gave the desired compound as light-yellow crystals (3.12 g, 26.3%). Yield. 26.3%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, 2H, $J = 6.4$ Hz), 7.81 (d, 2H, $J = 9.6$ Hz), 7.26 (m, 2H) ppm. EI-MS: *m/z* 286 [M^+]. Anal. Calcd for $C_{10}H_6Br_2$: C, 42.00; H, 2.11; Br, 55.88. Found: C, 41.8; H, 2.12.

1, 8-Bis(Pyrene-2-yl)naphthalene (BPyN).[3] 1, 8-dibromonaphthalene (0.50 g, 1.75 mmol), pyrene-2-boronate ester (1.72 g, 5.25 mmol), and $Pd(PPh_3)_4$ (0.175 mmol) and aqueous 2.0 M K_2CO_3 (10 mL) were mixed in a flask containing with nitrogen saturated toluene (100 mL). The reaction mixture was refluxed for 24 h under nitrogen. After it was cooled to room temperature, the reaction mixture was quenched with saturated sodium bicarbonate solution and extracted with toluene (100 mL × 2). The combined organic extracts were dried with anhydrous $MgSO_4$ and evaporated. The crude product was purified by column chromatography and recrystallization from hexane to afford the target compound as pale yellow crystals (2.43 g, 65%). m.p. 326 ˚C. Yield: 65%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, $J = 8.72$ Hz, 4H), 7.29 (d, $J = 8.72$ Hz, 4H), 7.52-7.54

(dd, *J* = 3.2 Hz, *J* = 3.64 Hz, 8H), 7.59–7.62 (m, 2H), 7.66–7.68 (dd, *J* = 3.2 Hz, *J* = 2.76 Hz, 4H), 8.11–8.13 (dd, *J* = 3.64 Hz, *J* = 3.68 Hz, 2H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$) δ 121.92, 123.19, 124.05, 125.02, 125.12, 125.91, 126.07, 126.44, 129.23, 129.49, 130.23, 131.05, 135.19, 140.18, 140.91, 145.58 ppm. EI-MS: *m/z* 529 [M^+]. Anal. Calcd for $C_{42}H_{24}$: calcd. C, 95.42; H, 4.58. Found: C, 95.40; H, 4.87.

References

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(2) R. M. Moriarty, J. S. Khosrowshahi, and T. M. Dalecki, *J. Chem. Soc., Chem. Commun.,* **1987**, 675.

(3) G.-Q. Li, Y. Yamamoto, and N. Miyaura, *Tetrahedron* **2011**, *67*, 6804.

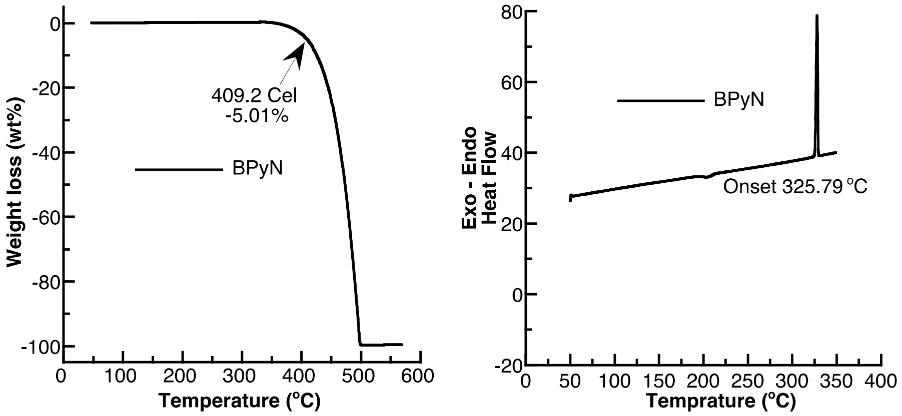

Figure S1. TGA trace (T_d = 409 ˚C) (left) and DSC curve of BPyN (no T_g was observed) (right).

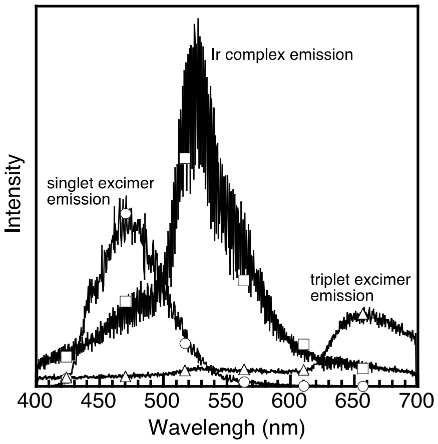

Figure S2. Phosphorescence spectra of BPyN for 0-10 ms (circle), BPyN with Ir(ppy)$_3$ for 0-12 ms (square), and BPyN with Ir(ppy)$_3$ for 2-10 ms (triangle), at 5 K.

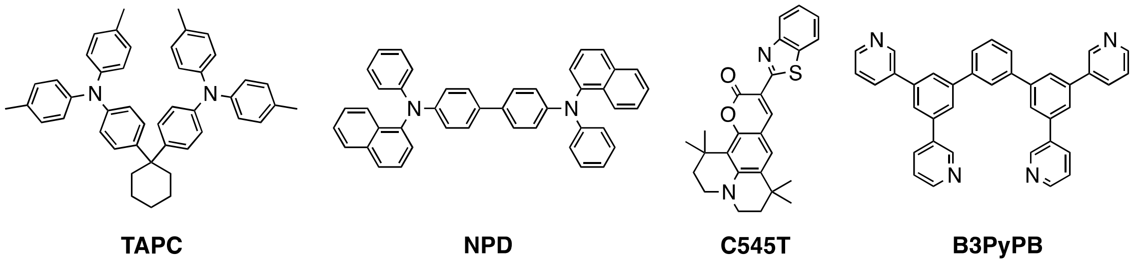

Figure S3. Chemical structure of TAPC, NPD, C545T, and B3PyPB.

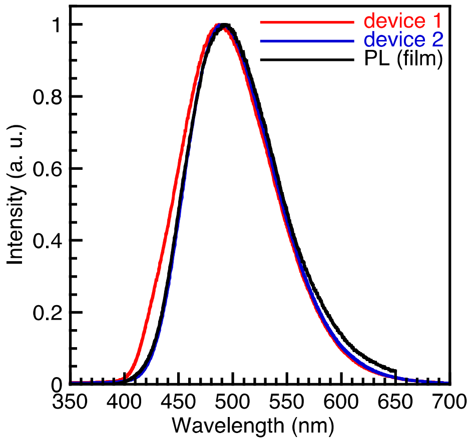

Figure S4. EL spectra of the devices 1-2 and PL spectra of BPyN thin film.

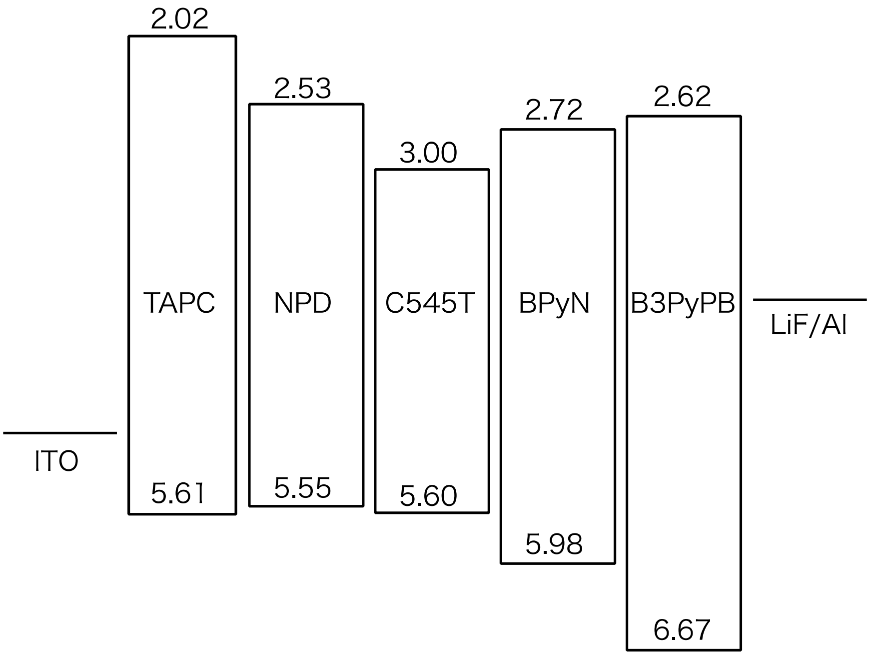

Figure S5. Energy level diagrams for the devices 1-3.