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Supporting information

A series of fluorinated phenylpyridine-based electron-transporters for blue phosphorescent OLEDs

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1. Experimental section

General considerations: Quantum chemical calculations were performed using the hybrid density functional theory (DFT) functional Becke and Hartree-Fock exchange and Lee Yang and Parr correlation (B3LYP) as implemented by the Gaussian 09 program packages.[1] Electrons were described by the Pople's 6-31G(d,p) and 6-311 + G(d,p) basis sets for molecular structure optimization and single-point energy calculations, respectively. ^{1}H NMR spectrum was recorded on JEOL 400 (400 MHz) spectrometer. Mass spectrum was 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}. UV-Vis spectra were measured using a Shimadzu UV-3150 UV-vis-NIR spectrophotometer. Photoluminescence spectra were measured using a FluroMax-2 (Jobin-Yvon-Spex) luminescence spectrometer. The ionization potential (I_p) was determined by a photoelectron yield spectroscopy (PYS) under the vacuum (~10^{-3} Pa).

Device Fabrication and Characterization: TAPC was purchased from TCI. TCTA and FIrpic were purchased from Chemipro Kasei. LiF was purchased from Furuuchi Chemical. TAPC, TCTA and FIrpic were purified by temperature-gradient sublimation in vacuum. Phosphorescent OLEDs were grown on glass substrates precoated with a 130-nm thick layer of indium-tin oxide (ITO) having a sheet resistance of 15 Ω/sq. The substrates were cleaned with ultrapurified water and organic solvents, and then dry-cleaned for 30 min by exposure to UV–ozone. The organic layers were deposited onto the ITO substrate under the vacuum (ca. 10^{-5} Pa), successively. Al was patterned using a shadow mask with an array of 2 mm × 2 mm openings without breaking the vacuum (ca. 10^{-5} Pa). The EL spectra were taken using an optical multichannel analyzer Hamamatsu Photonics PMA-11. The current density–voltage and luminance–voltage characteristics were measured using a Keithley source measure unit 2400 and a Minolta CS200 luminance meter, respectively.

2. DFT calculation

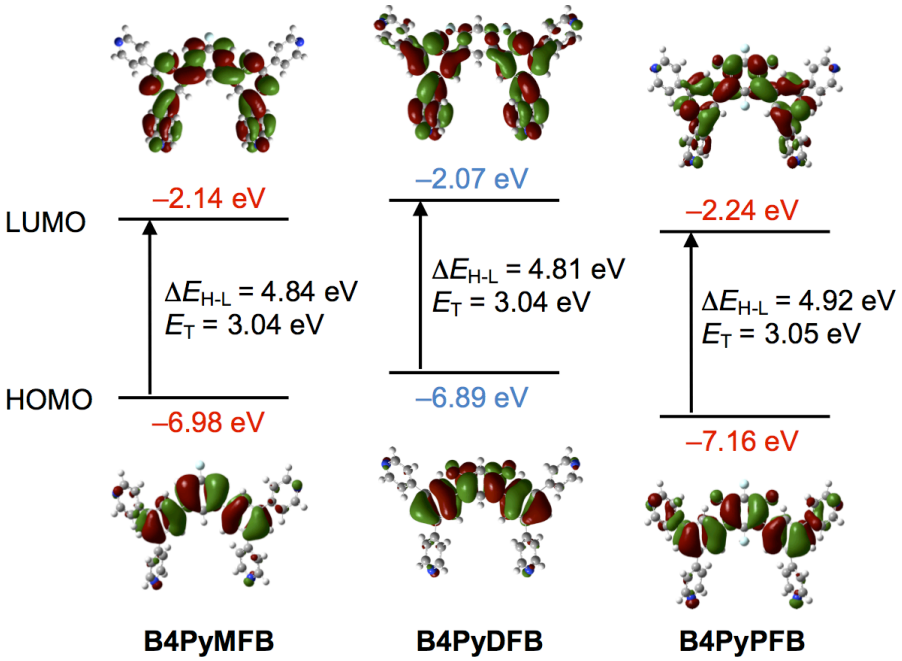
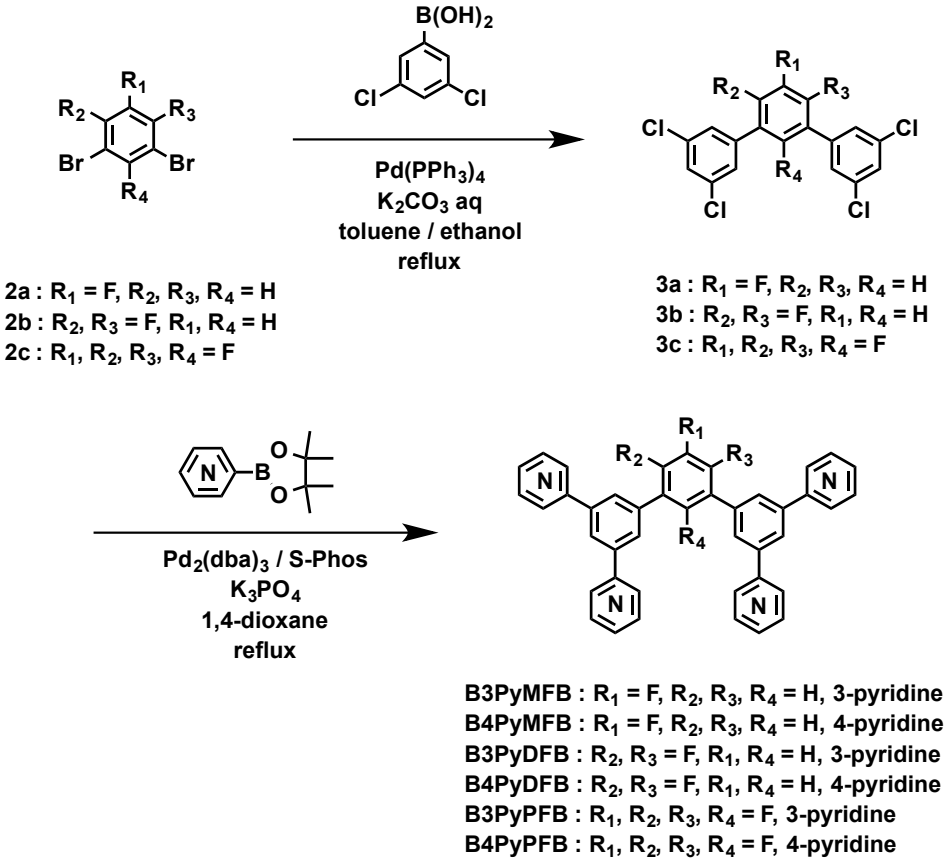


Figure S1. HOMO and LUMO distribution, energy levels, energy difference between HOMO and LUMO ($\Delta E_{H\text{-}L}$) and lowest triplet energy (E_T) of B4PyMFB, B4PyDFB and B4PyPFB.

3. Synthesis



Scheme S1. Synthetic route of fluorine-substituted phenylpyridine derivatives

Synthesis of 1,3-Bis(3,5-dichlorophenyl)-5-fluorobenzene (3a).
1,3-Dibromo-5-fluorobenzene (**2a**) (1.83 g, 7.2 mmol) and 3,5-dichlorophenyl boronic acid (2.78 g, 14.6 mmol) were added to a round bottom flask. Toluene (40 mL), ethanol (20 mL) and aqueous K_2CO_3 (2 M, 30 mL) were added and nitrogen (N_2) bubbled through the mixture for 1 hour. Then, $Pd(PPh_3)_4$ (0.50 g, 0.43 mmol) was added and the resultant mixture was stirred for 22 hours at reflux temperature under N_2 flow. The precipitate was filtered, and washed with water and methanol. The resulting off-white solid was dissolved in reflux toluene 100 mL, filtered through silica-gel pad (100 cc) and washed with toluene. After the clear filtrate was concentrated to 50 mL, the precipitate was collected, washed with methanol, and dried to afford **3a** (2.09 g, 75 %) as a white solid: ^{1}H-NMR (400 MHz, $CDCl_3$): δ= 7.47 (d, *J* = 1.8 Hz, 4H), 7.44 (t, *J* = 1.6 Hz, 1H), 7.40 (t, *J* = 1.8 Hz, 2H), 7.27 (d, *J* = 1.4 Hz, 2H) ppm; MS: *m/z* 386 $[M]^+$.

Synthesis of 1,5-Bis(3,5-dichlorophenyl)-2,4-difluorobenzene (3b).
1,5-Dibromo-2,4-difluorobenzene (**2b**)[2] (3.15 g, 11.6 mmol) and 3,5-dichlorophenyl boronic acid (4.46 g, 23.4 mmol) were added to a round bottom flask. Toluene (80 mL), ethanol (40 mL) and aqueous K_2CO_3 (2 M, 60 mL) were added and nitrogen (N_2) bubbled through the mixture for 1 hour. Then, $Pd(PPh_3)_4$ (1.62 g, 1.40 mmol) was added and the resultant mixture

was stirred for 61 hours at reflux temperature under N_2 flow. The precipitate was filtered, and washed with water and methanol. The resulting off-white solid was dissolved in reflux toluene 100 mL, filtered through silica-gel pad (100 cc) and washed with toluene. After the clear filtrate was concentrated and dried to afford **3b** (3.04 g, 65 %) as a white solid: ^{1}H-NMR (400 MHz, $(CD_3)_2SO$): δ= 7.05 (t, *J* = 8.6 Hz, 1H), 6.93 (d, *J* = 1.8 Hz, 4H), 6.87 (t, *J* = 1.8 Hz, 2H), 6.77 (t, *J* = 10.9 Hz, 1H) ppm; MS: *m/z* 404 $[M]^+$.

Synthesis of 1,3-Bis(3,5-dichlorophenyl)-2,4,5,6-tetrafluorobenzene (3c).
1,3-Dibromo-2,4,5,6-tetrafluorobenzene (**2c**) (10.0 g, 32.5 mmol) and 3,5-dichlorophenyl boronic acid (12.5 g, 35.7 mmol) were added to a round bottom flask. Toluene (200 mL), ethanol (100 mL) and aqueous K_2CO_3 (2 M, 130 mL) were added and nitrogen (N_2) bubbled through the mixture for 1 hour. Then, $Pd(PPh_3)_4$ (2.25 g, 1.95 mmol) was added and the resultant mixture was stirred for 20 hours at reflux temperature under N_2 flow. The precipitate was filtered, and washed with water and methanol. The resulting off-white solid was dissolved in reflux toluene 100 mL, filtered through silica-gel pad (300 cc) and washed with toluene. After the clear filtrate was concentrated to 50 mL, the precipitate was collected, washed with methanol, and dried to afford **3c** (11.6 g, 81 %) as a white solid: ^{1}H-NMR (400 MHz, $CDCl_3$): δ= 7.46 (t, *J* = 2.0 Hz, 2H), 7.34 (s, 4H) ppm; MS: *m/z* 438 $[M]^+$.

Synthesis of B3PyMFB.
3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (3.54 g, 17.2 mmol) and **3a** (1.33 g, 3.44 mmol) were added to a round bottom flask. 1,4-Dioxane (43 mL) and aqueous K_3PO_4 (1.35 M, 30 mL) were added and nitrogen (N_2) bubbled through the mixture for 1 hour. Then, $Pd_2(dba)_3$ (0.064 g, 0.07 mmol) and 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (S-Phos) (0.059 g, 0.143 mmol) were added and the resultant mixture was stirred for 23 hours at reflux temperature under N_2 flow. The precipitate was filtered, and washed with water and methanol. The resulting off-white solid was purified by chromatography on silica gel (eluent: $CHCl_3/CH_3OH$ = 200/1, 100/1 to 100/5 v/v) to afford **B3PyMFB** (1.64 g, 86 %) as a white solid: ^{1}H-NMR (400 MHz, $CDCl_3$): δ= 8.95 (d, *J* = 2.3 Hz, 4H), 8.66 (dd, *J* = 5.0, 1.4 Hz, 4H), 7.98 (dt, *J* = 8.0, 1.9 Hz, 4H), 7.84 (d, *J* = 1.4 Hz, 4H), 7.79 (t, *J* = 1.6 Hz, 2H), 7.72 (s, 1H), 7.44 (dd, *J* = 7.9, 4.8 Hz, 6H) ppm; MS: *m/z* 557 $[M]^+$; Anal calcd for $C_{38}H_{25}FN_4$: C 81.99, H 4.53, N 10.07%; found: C 82.03, H 4.59, N 10.10%.

Synthesis of B4PyMFB.
4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (2.66 g, 13.0 mmol) and **3a** (1.0 g, 2.59 mmol) were added to a round bottom flask. 1,4-Dioxane (32 mL) and aqueous K_3PO_4 (1.35 M, 24 mL) were added and nitrogen (N_2) bubbled through the mixture for 1 hour. Then, $Pd_2(dba)_3$ (0.049 g, 0.053 mmol) and 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (S-Phos) (0.044 g, 0.108 mmol) were added and the resultant mixture was stirred for 61 hours at reflux temperature under N_2 flow. The precipitate was filtered, and washed with water and methanol. The resulting off-white solid was purified by chromatography on silica gel (eluent: $CHCl_3/CH_3OH$ = 100/5 to 100/10 v/v) to afford **B4PyMFB** (0.385 g, 27 %) as a white solid: ^{1}H-NMR (400 MHz, $CDCl_3$): δ= 8.73 (d, *J* = 4.5 Hz, 8H), 7.95 (s, 1H), 7.90 (d, *J* = 3.2 Hz,

4H), 7.68 (d, *J* = 9.5 Hz, 2H), 7.60 (d, *J* = 4.4 Hz, 8H), 7.44 (d, *J* = 9.1 Hz, 2H) ppm; MS: *m/z* 557 $[M]^+$; Anal calcd for $C_{38}H_{25}FN_4$: C 81.99, H 4.53, N 10.07%; found: C 81.64, H 4.34, N 9.86%.

Synthesis of B3PyDFB.

3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (3.82 g, 18.6 mmol) and **3b** (1.50 g, 3.71 mmol) were added to a round bottom flask. 1,4-Dioxane (46 mL) and aqueous K_3PO_4 (1.35 M, 19 mL) were added and nitrogen (N_2) bubbled through the mixture for 1 hour. Then, $Pd_2(dba)_3$ (0.07 g, 0.076 mmol) and 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (S-Phos) (0.062 g, 0.152 mmol) were added and the resultant mixture was stirred for 40 hours at reflux temperature under N_2 flow. The precipitate was filtered, and washed with water and methanol. The resulting off-white solid was purified by chromatography on silica gel (eluent: $CHCl_3/CH_3OH$ = 100/1, 100/2, 100/5 to 100/10 v/v) to afford **B3PyDFB** (1.95 g, 92 %) as a white solid: ^{1}H-NMR (400 MHz, $CDCl_3$): δ= 8.93 (d, *J* = 2.3 Hz, 4H), 8.65 (dd, *J* = 4.8, 1.6 Hz, 4H), 7.97 (dt, *J* = 7.8, 2.1 Hz, 4H), 7.78 (s, 6H), 7.68 (t, *J* = 8.2 Hz, 1H), 7.40-7.43 (m, 4H), 7.16 (t, *J* = 10.1 Hz, 1H) ppm; MS: *m/z* 576 $[M+H]^+$.

Synthesis of B4PyDFB.

4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (3.91 g, 19.0 mmol) and **3b** (1.53 g, 3.79 mmol) were added to a round bottom flask. 1,4-Dioxane (46 mL) and aqueous K_3PO_4 (1.35 M, 19 mL) were added and nitrogen (N_2) bubbled through the mixture for 1 hour. Then, $Pd_2(dba)_3$ (0.071 g, 0.077 mmol) and 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (S-Phos) (0.063 g, 0.154 mmol) were added and the resultant mixture was stirred for 19 hours at reflux temperature under N_2 flow. The precipitate was filtered, and washed with water and methanol. The resulting off-white solid was purified by chromatography on silica gel (eluent: $CHCl_3/CH_3OH$ = 100/1.5, 100/2, 100/3, 100/5 to 100/10 v/v) to afford **B4PyDFB** (2.1 g, 96 %) as a white solid: ^{1}H-NMR (400 MHz, $CDCl_3$): δ= 8.73 (d, *J* = 6.0 Hz, 8H), 7.89 (s, 2H), 7.86 (s, 4H), 7.66 (t, *J* = 8.4 Hz, 1H), 7.59 (d, *J* = 6.0 Hz, 8H), 7.18 (t, *J* = 10.0 Hz, 1H) ppm; MS: *m/z* 576 $[M+H]^+$; Anal calcd for $C_{38}H_{25}FN_4$: C 79.43, H 4.21, N 9.75%; found: C 79.25, H 4.13, N 9.75%.

Synthesis of B3PyPFB.

3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (17.06 g, 83.1 mmol) and **3c** (7.04 g, 16.0 mmol) were added to a round bottom flask. 1,4-Dioxane (200 mL) and aqueous K_3PO_4 (1.35 M, 80 mL) were added and nitrogen (N_2) bubbled through the mixture for 1 hour. Then, $Pd_2(dba)_3$ (0.30 g, 0.327 mmol) and 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (S-Phos) (0.274 g, 0.667 mmol) were added and the resultant mixture was stirred for 20 hours at reflux temperature under N_2 flow. The precipitate was filtered, and washed with water and methanol. The resulting off-white solid was purified by chromatography on silica gel (eluent: $CHCl_3/CH_3OH$ = 100/0, 100/1, 100/3, 100/5 to 100/10 v/v) to afford **B3PyPFB** (5.73 g, 59 %) as a white solid: ^{1}H-NMR (400 MHz, $CDCl_3$): δ= 8.94 (dd, *J* = 2.4, 0.8 Hz, 4H), 8.67 (dd, *J* = 4.8, 1.6 Hz, 4H), 7.99-7.93 (m, 4H), 7.85 (t, *J* = 1.6 Hz, 2H), 7.73 (s, 4H), 7.45-7.40 (m, 4H) ppm; MS: *m/z* 611 $[M]^+$; Anal calcd for $C_{38}H_{25}FN_4$: C 74.75, H 3.63, N 9.18%;

found: C 74.46, H 3.38, N 9.10%.

Synthesis of B4PyPFB.

4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (2.33 g, 11.4 mmol) and **3c** (1.0 g, 2.27 mmol) were added to a round bottom flask. 1,4-Dioxane (30 mL) and aqueous K_3PO_4 (1.35 M, 11 mL) were added and nitrogen (N_2) bubbled through the mixture for 1 hour. Then, $Pd_2(dba)_3$ (0.0424 g, 0.0463 mmol) and 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (S-Phos) (0.0388 g, 0.0946 mmol) were added and the resultant mixture was stirred for 48 hours at reflux temperature under N_2 flow. The precipitate was filtered, and washed with water and methanol. The resulting off-white solid was purified by chromatography on silica gel (eluent: $CHCl_3/CH_3OH$ = 100/1, 100/1.5, 100/3, 100/5 to 100/10 v/v) to afford **B4PyPFB** (0.768 g, 55 %) as a white solid: ^{1}H-NMR (400 MHz, $CDCl_3$): δ= 8.73 (d, *J* = 5.9 Hz, 8H), 7.93 (d, *J* = 1.8 Hz, 2H), 7.80 (s, 4H), 7.57 (dd, *J* = 4.4, 1.6 Hz, 8H) ppm; MS: *m/z* 611 $[M]^+$.

4. UV-PL spectra

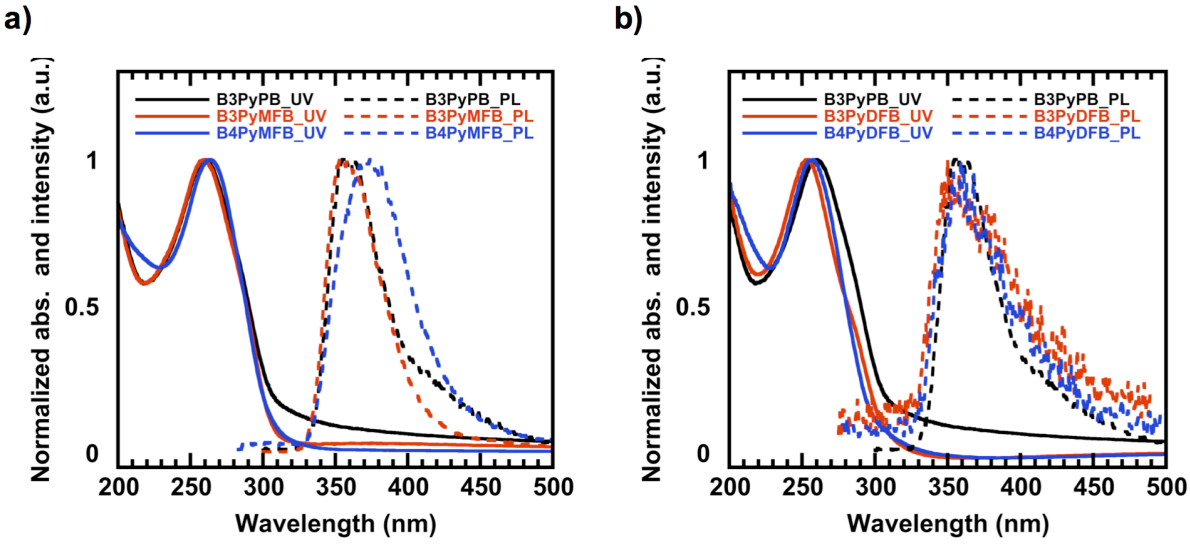


Figure S2. UV-vis absorption and photluminescence spectra of a) BPyMFB and b) BPyDFB. B3PyPB is used as reference.

5. X-ray Crystallographic Structure Determination for B4PyMFB

X-ray diffraction data for B4PyMFB was collected on a Rigaku Saturn 724 CCD diffractometer with Mo-*K*α radiation (λ = 0.71075 Å) at 93(2) K. Single crystal of B4PyMFB [C_{38} H_{25} F N_4, Mw = 556.62] suitable for X-ray analysis were grown by slow gradient sublimation, and a colourless crystal with dimensions 0.10 × 0.05 × 0.05 mm was selected for intensity measurements. The unit cell was orthorhombic with the space group *P* m n 21. Lattice constants with Z = 2, D_{calced} = 1.387 g cm^{-3}, μ = 0.087 mm^{-1}, *F*(000) = 580, and 2θmax = 53.0° were *a* = 33.005(12), *b* = 3.7442(13), *c* = 10.782(4) Å, α = 90°, β = 90°, γ = 90°, and V = 1332.4(8) $Å^3$. A total of 15232 reflections were collected, of which 2817 reflections were independent (R_{int} = 0.0280). Structure was refined to final R_1 = 0.0335 for 2817 data [I>2σ(I)] with 199 parameters and wR_2 = 0.1054 for all data, GOF = 1.107, and residual electron density max./min. = 0.317/–0.270 e$Å^{-3}$. The ORTEP drawing is shown in Figure S3, and the crystal data and structure refinement are listed in Table S1.

Data collection, cell refinement, and data reduction were conducted using the CrystalClear-SM Expert software[3]. The structure was solved by direct methods using the program SHELXS-97[4] and refined by full matrix least squares methods on F^2 using SHELXL-97[5]. All materials for publication were prepared by Yadokari-XG 2009 software[6]. All non-hydrogen atoms were refined anisotropically. The positions of all hydrogen atoms were calculated geometrically and refined a riding model.

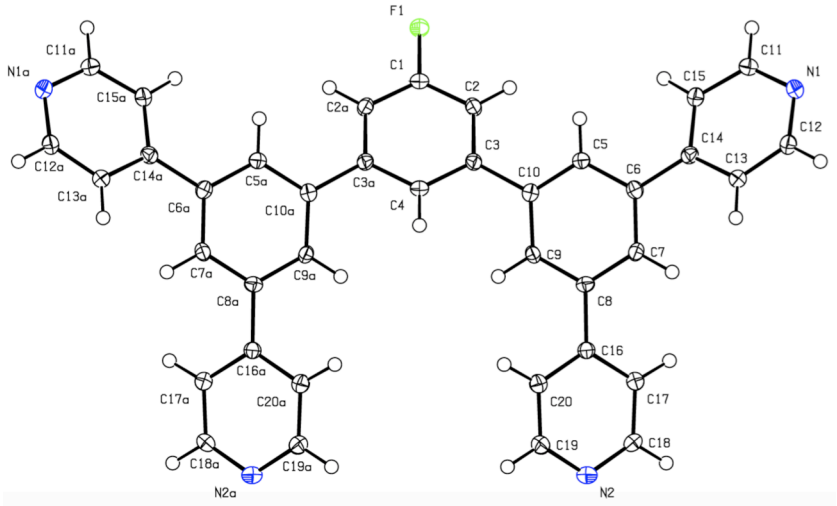


Figure S3. ORTEP diagram of B4PyMFB with thermal ellipsoids at 50% probability.

Table S1. Crystal data and structure refinement for B4PyMFB.

Empirical formula	C_{38} H_{25} F N_4	
Formula weight	556.62	
Temperature	93 K	
Wavelength	0.71075 Å	
Crystal system	Orthorhombic	
Space group	P m n 21	
Unit cell dimensions	a = 33.005(12) Å	α= 90°
	b = 3.7442(13) Å	β= 90°
	c = 10.782(4) Å	γ = 90°
Volume	1332.4(8) Å^3	
Z	2	
Density (calculated)	1.387 g/cm^3	
Absorption coefficient	0.087 mm^{-1}	
F(000)	580	
Crystal size	0.10 × 0.05 × 0.05 mm^3	
Theta range for data collection	1.99 to 26.50°	
Index ranges	–41<=h<=41, –4<=k<=4, –13<=l<=13	
Reflections collected	15232	
Independent reflections	2817 [R(int) = 0.0280]	
Completeness to theta = 26.50°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.000 and 0.906	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2817 / 1 / 199	
Goodness-of-fit on F^2	1.107	
Final R indices [I>2sigma(I)]	R_1 = 0.0335, wR_2 = 0.0915	
R indices (all data)	R_1 = 0.0373, wR_2 = 0.1054	
Largest diff. peak and hole	0.317 and –0.270 eÅ^{-3}	

6. Electron mobility

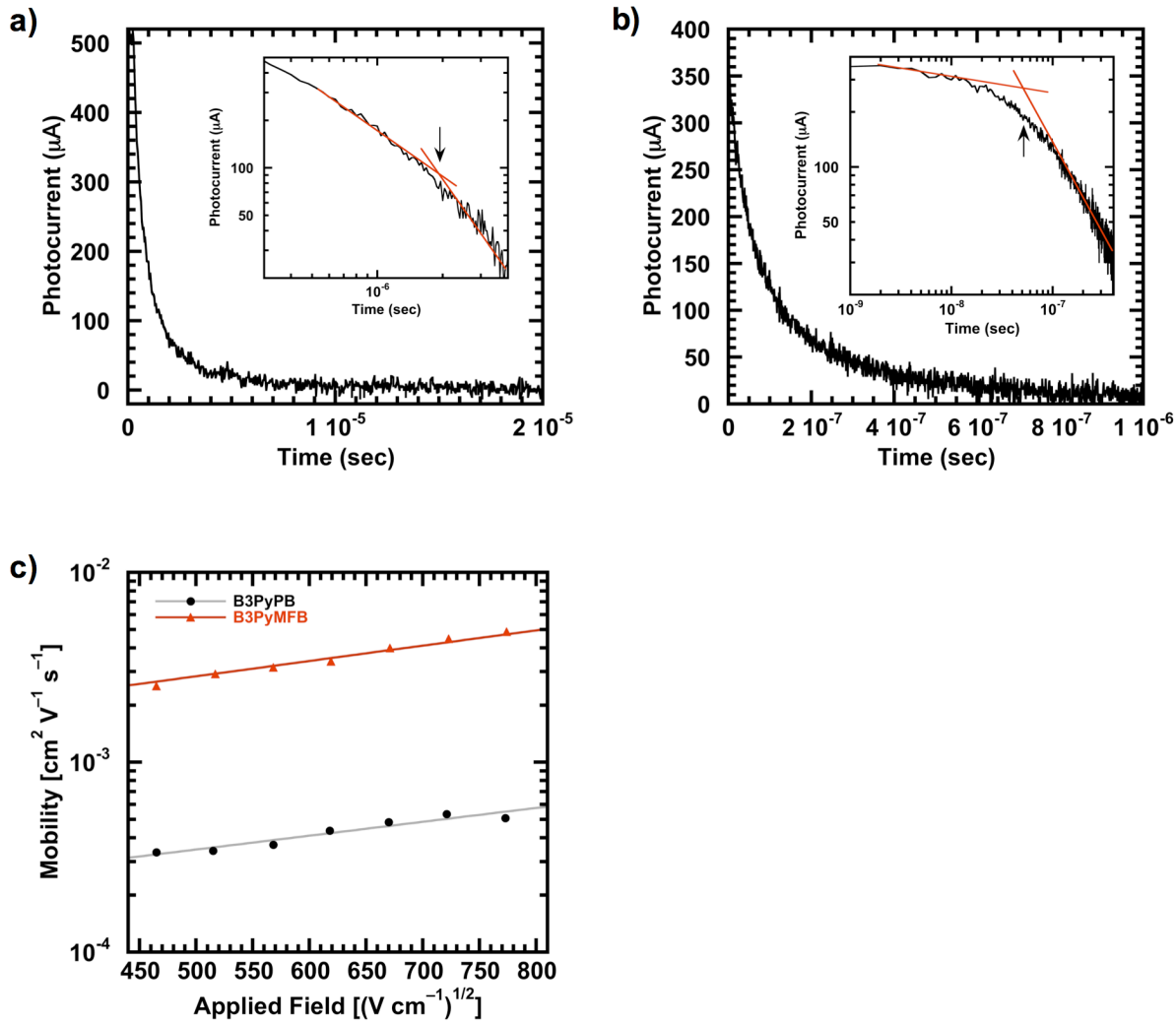


Figure S4. Representative transient TOF of electrons at room temperature: a) B3PyMFB at an electric field of 6.0×10^5 V cm^{-1}; b) B3PyMFB at an electric field of 5.2×10^5 V cm^{-1}. The inset is double logarithmic plot, c) field-dependent mobility of B3PyMFB and B3PyPB.

7. OLED devices

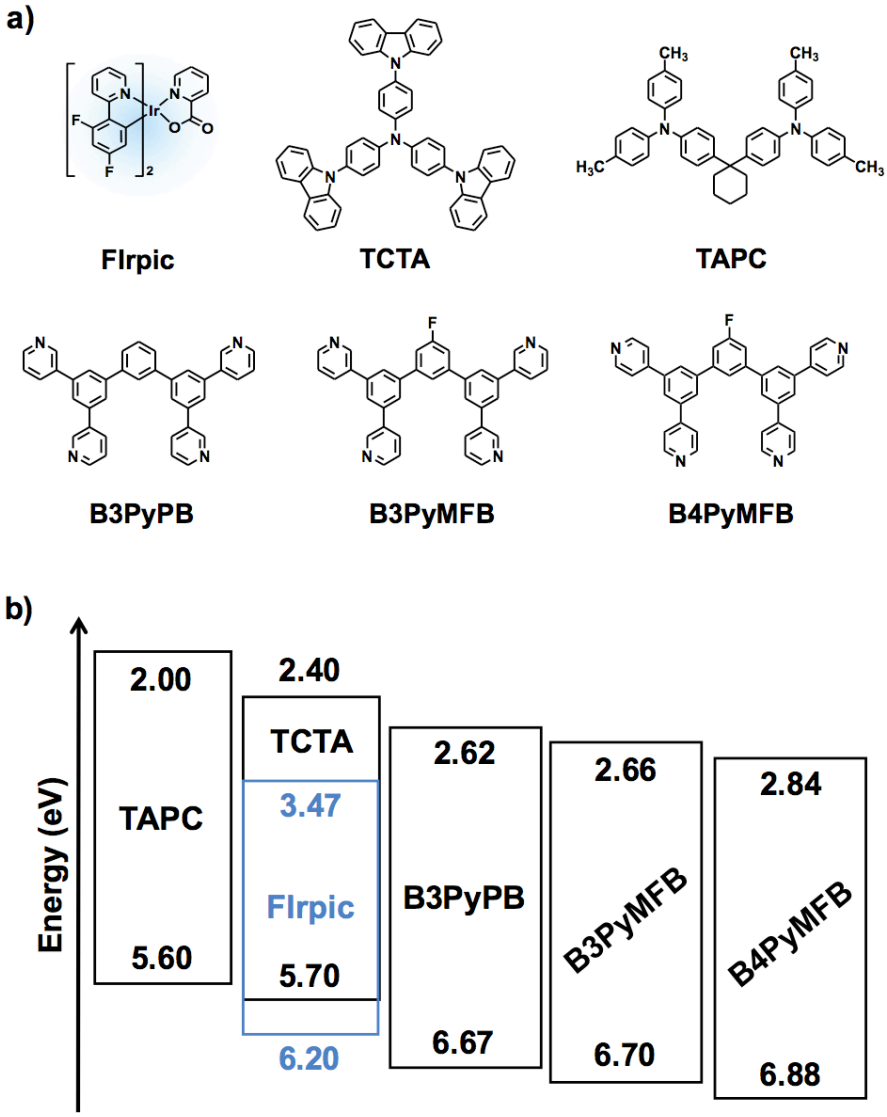


Figure S5. a) Chemical structures, b) energy diagram of blue devices.

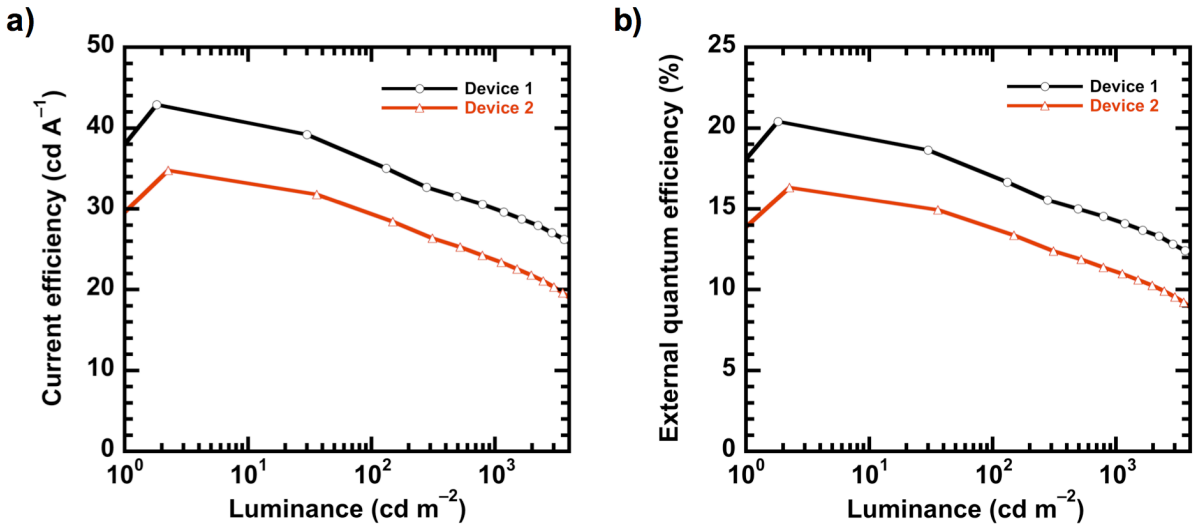


Figure S6. Performance of **Device 1** and **2**: a) current efficiency–voltage (*CE*–*V*) characteristics; b) external quantum efficiency–luminance (η_{ext}–*L*) characteristics.

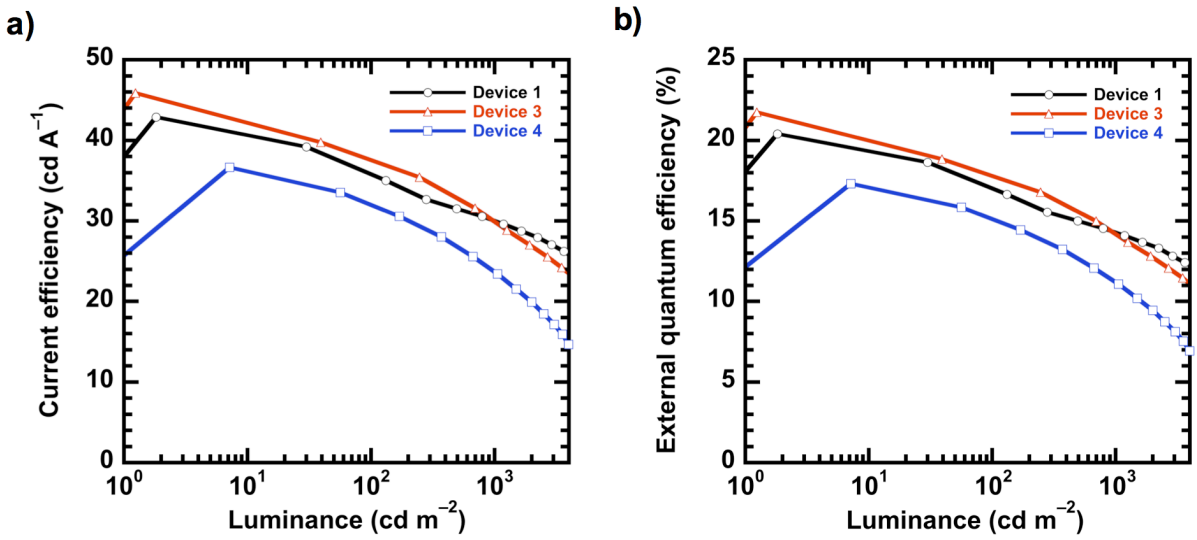


Figure S7. Performance of **Device 1, 3** and **4**: a) *CE*–*V* characteristics; b) η_{ext}–*L* characteristics.

8. References

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