High-efficiency non-doped deep-blue fluorescent organic light-emitting diodes based on carbazole/phenanthroimidazole derivatives

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Contents:

1. Synthesis Procedures
2. Time-Resolved Transient PL Decay
3. Cyclic Voltammetry of 2FPPICz and 2FPPIPCz
4. Analyses of Natural Transition Orbitals (NTOs)
5. Carrier Transporting Characteristics
6. The Devices Lifetime
1. Synthesis Procedures

Fig. S1. Synthesis routes and chemical structures of 2FPPICz and 2FPPIPcZ.

1.1 Synthesis of 2-(4-bromophenyl)-1-(3,5-difluorophenyl)-1H-phenanthro[9,10-d]imidazole (2FPPIBr).

2FPPIBr is synthesized using a one-pot cyclization reaction by the method in the literature.

1.2 Synthesis of 2-(4-(9H-carbazol-9-yl)phenyl)-1-(3,5-difluorophenyl)-1H-phenanthro[9,10-d]imidazole (2FPPICZ).

2FPPIBr (2.91 g, 6 mmol), 9H-carbazole (1.1 g, 6.6 mmol), Pd(dba)$_2$ (172 mg, 0.3 mmol), K$_2$CO$_3$ (2.49 g, 18 mmol) and 100 mL toluene were refluxed in nitrogen atmosphere for 20 hours. After cooled to room temperature, the reaction system was poured into water and stirred for 15 min to dissolve K$_2$CO$_3$, and then separated by vacuum suction filtration. Due to the poor solubility of the filter cake, it was purified by vacuum sublimation directly to give the final product. Yield 69% (2.37 g), white powder.

1H NMR (500 MHz, THF-d8) $\delta$ 8.88 (d, J = 8.4 Hz, 1H), 8.86 – 8.82 (m, 1H), 8.80 (d, J = 8.3 Hz, 1H), 8.13 (d, J = 7.8 Hz, 2H), 7.97 (d, J = 8.4 Hz, 2H), 7.72 (t, J = 7.4 Hz, 1H), 7.69 – 7.62 (m, 3H), 7.61 – 7.52 (m, 3H), 7.45 (d, J = 8.3 Hz, 3H), 7.37 (q, J = 7.1 Hz, 3H), 7.30 (d, J = 8.2 Hz, 1H), 7.24 (t, J = 7.4 Hz, 2H). EI-ITMS, m/z: 571.21 [M$^+$]. Calcd: 571.19. Elem. Anal. Calcd. (%) for C$_{39}$H$_{23}$F$_2$N$_3$: C, 81.95; H, 4.06, N, 7.35. Found: C, 81.82; H, 4.22; N, 7.35.

1.3 Synthesis of 2-(4′-(9H-carbazol-9-yl)-[1,1′-biphenyl]-4-yl)-1-(3,5-difluorophenyl)-1H-phenanthro[9,10-d]imidazole (2FPPIPcZ).

2FPPIBr (2.91 g, 6 mmol), (4-(9H-carbazol-9-yl)phenyl)boronic acid (1.90 g, 6.6 mmol), Pd(PPh$_3$)$_4$ (277 mg, 0.24 mmol), 2 mol L$^{-1}$ K$_2$CO$_3$ (3mL 6 mmol.), tetrabutylammonium bromide (829 g, 0.6 mmol) and toluene were refluxed in nitrogen atmosphere for 12 hours. After cooled to room temperature, the reaction system was poured into water and extracted with dichloromethane. Then the crude product was purified via column chromatography using dichloromethane and ethyl acetate as eluent. Yield 92% (3.58 g), white powder. 1H NMR (500 MHz, THF-d8) $\delta$ 8.87 (d, J = 8.4 Hz, 1H), 8.83 (dd, J = 7.9, 1.4 Hz, 1H), 8.79 (d, J = 8.4 Hz, 1H), 8.15 (d, J = 7.8 Hz, 2H), 8.03 – 7.94 (m, 2H), 7.86 – 7.76 (m, 4H), 7.75 – 7.67 (m, 3H), 7.67 – 7.58 (m, 1H), 7.58 – 7.49 (m, 3H), 7.49 – 7.41 (m, 3H), 7.37 (dt, J = 11.7, 7.3 Hz, 3H), 7.30 (d, J = 8.1 Hz, 1H), 7.24 (t, J = 7.4 Hz, 2H). EI-ITMS, m/z: 647.23 [M$^+$]. Calcd: 647.22. Elem. Anal. Calcd. (%) for C$_{45}$H$_{27}$F$_2$N$_3$: C, 83.44; H, 4.20, N, 6.49. Found: C, 83.37; H, 4.69; N, 6.47.
2. Time–Resolved Transient PL Decay.

Fig. S2. Transient PL decay profiles of 2FPPICz (a) and 2FPPIPCz (b) in thin films.

3. Cyclic Voltammetry of 2FPPICz and 2FPPIPCz.

Fig. S3. Cyclic voltammograms of 2FPPICz and 2FPPIPCz.
4. Analyses of Natural Transition Orbitals (NTOs).

Fig. S4. NTOs of $S_0 \rightarrow S_1$ transition. $f$ represents oscillator strength.

5. Carrier Transporting Characteristics.

Fig. S5. Current density-voltage curves of HOD and EOD of 2FPPICz (a) and 2FPPIPCz (b).
6. The Devices Lifetime.

**Fig. S6.** The lifetime characterization of devices B1 and B2. (a) Under the current density of 40 mA/cm$^2$ with the initial luminance of 510 cd/m$^2$ and 1800 cd/m$^2$ for devices B1 and B2, respectively. (b) Under the current density of 87.5 mA/cm$^2$ with the initial luminance of 980 cd/m$^2$ and 3800 cd/m$^2$ for devices B1 and B2, respectively.