

Supporting information

CN engineered electron transport type hosts for high efficiency and extended lifetime in blue thermally activated delayed fluorescent organic light-emitting diodes

Sung Yong Byeon, Kyung Hyung Lee, *and* Jun Yeob Lee *

School of Chemical Engineering, Sungkyunkwan University
2066, Seobu-ro, Jangan-gu, Suwon-si, Gyeonggi-do, 16419, Korea
E-mail : leej17@skku.edu

Experimental

General information

3-Bromo-2-fluorobenzonitrile, tetrakis(triphenylphosphine)palladium(0), 9*H*-carbazole-3-carbonitrile, 9*H*-carbazole-3,6-dicarbonitrile, dibenzo[*b,d*]furan-4-ylboronic acid (P&H tech), potassium carbonate, *N,N*-dimethylformamide (DMF) (Duksan Sci. Co.), 1-bromo-2-fluorobenzene (Thermo Fisher Scientific, Inc), methylene chloride (MC) and n-hexane (HEX) (Samchun pure chemical Co. Ltd.) and dimethylsulfoxide-*d*₆ (Sigma-Aldrich Co. LLC.) were used without further purification. Tetrahydrofuran (THF) (Samchun pure chemical Co. Ltd.) was distilled over sodium and calcium hydride.

The ¹H and ¹³C nuclear magnetic resonance (NMR) spectra were recorded on a Avance-500 (Bruker, 500 MHz) spectrometer. The ultraviolet-visible (UV-vis) spectra were obtained using UV-vis spectrophotometer (JASCO, V-730), and the photoluminescence (PL) spectra were recorded on a fluorescence spectrophotometer (PerkinElmer, LS-55). The energy levels of highest occupied molecular orbital and lowest unoccupied molecular orbital were estimated using a cyclic voltammetry (Ivium Tech., Iviumstat). The mass spectra were recorded using a Advion, Expression^L CMS spectrometer in APCI mode.

Synthesis

3-(Dibenzo[*b,d*]furan-4-yl)-2-fluorobenzonitrile

Dibenzo[*b,d*]furan-4-ylboronic acid (1.8 g, 8.49 mmol) and 3-bromo-2-fluorobenzonitrile (1.9 g, 9.35 mmol) were poured into RB and dissolved in THF (50 ml). The 20 ml aqueous solution of potassium carbonate (3.5 g, 25.5 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.3 g, 0.25 mmol) were poured into the RB and the reaction mixture was heated up with stirring to reflux temperature for 12 h. Then the reaction mixture was cooled to room temperature and extracted using MC/water. The organic layer was collected and dehydrated using magnesium sulfate (MgSO₄). A white solid was obtained after further purification using column chromatography with an eluent of MC:HEX.

Yield 70 %. ¹H NMR (300 MHz, DMSO-*d*₆): δ 8.29 (d, 1H, J=7.5Hz), 8.23 (d, 1H, J=7.8Hz), 8.13-8.06 (m, 2H), 7.74 (d, 1H, J=8.1Hz), 7.66-7.53 (m, 4H), 7.45 (t, 1H, J=7.5Hz), MS (APCI) m/z 287.2 [(M+H)⁺].

9-(2-Bromophenyl)-9H-carbazole-3,6-dicarbonitrile

9H-carbazole-3,6-dicarbonitrile (3.0 g, 13.81 mmol) and 1-bromo-2-fluorobenzene (3.1 g, 17.95 mmol) were poured into a pressure tube and dissolved in DMF (15 ml). The cesium carbonate (6.8 g, 20.72 mmol) were poured into the pressure tube and the reaction mixture was heated to 130 °C with stirring for 12 h. The reaction mixture was cooled to room temperature and precipitated with excess amount of water. The obtained precipitate through the filter was dissolved in MC and dehydrated using MgSO₄. A white solid was obtained after further purification using column chromatography with an eluent of MC:HEX.

Yield 75%. ¹H NMR (300 MHz, DMSO-*d*₆): δ 8.94 (s, 2H), 8.01 (d, 1H, J=8.1Hz), 7.88 (d, 2H, J=8.7Hz), 7.77-7.60 (m, 3H), 7.22 (d, 2H, J=8.4Hz), MS (APCI) m/z 373.3 [(M+H)⁺].

9-(2-Cyano-6-(dibenzo[*b,d*]furan-4-yl)phenyl)-9*H*-carbazole-3-carbonitrile (4DBF-BNCZ)

3-(Dibenzo[*b,d*]furan-4-yl)-2-fluorobenzonitrile (1.0 g, 3.48 mmol) and 9*H*-carbazole-3-carbonitrile (0.9 g, 4.53 mmol) were poured into a pressure tube and dissolved in DMF (10 ml). The cesium carbonate (1.7 g, 5.22 mmol) were poured into the pressure tube and the reaction mixture was heated to 130 °C with stirring for 12 h. The reaction mixture was cooled to room temperature and precipitated with excess amount of water. The obtained precipitate through the filter was dissolved in MC and dehydrated using MgSO₄. A white solid was obtained after further purification using column chromatography with an eluent of MC:HEX. The white solid was recrystallized in toluene and vacuum sublimated to obtain highly pure product.

Yield 75 %. ¹H NMR (500 MHz, DMSO-*d*₆): δ 8.58 (s, 1H), 8.36 (d, 1H, J=8.0Hz), 8.25 (d, 1H, J=8.0Hz), 8.08-8.04 (m, 2H), 7.91 (d, 1H, J=7.5Hz), 7.85 (d, 1H, J=7.5Hz), 7.73 (d, 1H, J=8.5Hz), 7.41 (d, 1H, J=8.5Hz), 7.39-7.34 (m, 2H), 7.29 (d, 1H, J=7.5Hz), 7.25 (d, 1H, J=7.5Hz), 7.23-7.19 (m, 2H), 7.15 (t, 1H, J=7.5Hz), 7.03 (d, 1H, J=8.5Hz) ¹³C NMR (125MHz, DMSO-*d*₆): δ 154.8, 152.0, 141.8, 140.5, 137.7, 137.3, 136.3, 134.9, 130.8, 129.1, 127.6, 127.5, 127.3, 125.6, 123.3, 123.1, 122.9, 122.7, 121.4, 121.4, 121.1, 121.0, 120.5, 119.8, 115.8, 113.2, 111.4, 110.9, 110.6. MS (APCI) m/z 459.9 [(M+H)⁺].

9-(2-(Dibenzo[*b,d*]furan-4-yl)phenyl)-9*H*-carbazole-3,6-dicarbonitrile (4DBF-PCZ)

9-(2-Bromophenyl)-9*H*-carbazole-3,6-dicarbonitrile (1.0 g, 2.69 mmol) and dibenzo[*b,d*]furan-4-ylboronic acid (0.6 g, 2.96 mmol) were poured into RB and dissolved in THF (30 ml). The 15 ml aqueous solution of potassium carbonate (1.1 g, 0.81 mmol) and

tetrakis(triphenylphosphine)palladium(0) (0.2 g, 0.13 mmol) were poured into the RB and the reaction mixture was heated up with stirring to reflux temperature for over night. Then the reaction mixture was cooled to room temperature and extracted using MC/water. The organic layer was collected and dehydrated using MgSO₄. A white solid was obtained after further purification using column chromatography with an eluent of MC:HEX.

Yield 70 %. ¹H NMR (500 MHz, DMSO-*d*6): δ 8.86 (s, 2H), 7.92 (d, 1H, J=7.0Hz), 7.89-7.81 (m, 5H), 7.76 (d, 2H, J=8.5Hz), 7.41-7.39 (m, 3H), 7.32 (t, 1H, J=7.3Hz), 7.21 (t, 2H, J=7.8Hz), 6.83 (d, 1H, J=8.0Hz) ¹³C NMR (125MHz, DMSO-*d*6): δ 154.6, 152.1, 142.8, 134.8, 133.3, 132.6, 130.4, 130.2, 130.0, 129.1, 127.8, 127.5, 126.1, 123.3, 123.1, 122.9, 122.7, 122.0, 121.5, 121.1, 120.9, 119.6, 111.9, 110.5, 102.6. MS (APCI) m/z 459.8 [(M+H)⁺].

Device fabrication and measurements

Blue TADF devices were fabricated based on the device structure of ITO (50 nm)/DNTPD (40 nm)/BPBPA (10 nm)/PCZAc (10 nm)/host:5CzCN (30 nm : 5 wt%)/DBFTrz (5 nm)/NAPIm (20 nm)/LiF (1.5 nm)/Al (200 nm), where ITO is indium tin oxide, DNTPD is *N,N'*-diphenyl-*N,N'*-bis-[4-(phenyl-*m*-tolyl-amino)-phenyl]-biphenyl-4,4'-diamine, BPBPA is *N,N,N',N'*-tetra[(1,10-biphenyl)-4-yl]-(1,10-biphenyl)-4,4'-diamine, PCZAc is 9,9-dimethyl-10-(9-phenyl-9*H*-carbazol-3-yl)-9,10-dihydroacridine, DBFTrz is 2,8-bis(4,6-diphenyl-1,3,5-triazin-2-yl)dibenzo[*b,d*]thiophene, and NAPIm is 9,10-di(naphthalene-2-yl)anthracen-2-yl-(4,1-phenylene)(1-phenyl-1*H*benzo[*d*]imidazole).

The electron only device structure was ITO (50 nm)/PEDOT:PSS (60 nm)/TSPO1 (10 nm)/host (25 nm)/TSPO1 (5 nm)/TPBi (40 nm)/LiF (1.5 nm)/Al (200 nm), where PEDOT:PSS is poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) and TSPO1 is diphenylphosphine oxide-4-(triphenylsilyl)phenyl.

Vacuum thermal evaporation process was used in the device fabrication, and the devices were encapsulated for the device test. Device performance analysis was carried out using measurement system of Keithley 2400 and CS 1000 (Konica Minolta Inc.) spectroradiometer. Lifetime test was carried out in dark condition using Polaronix (McScience Co.) lifetime measurement system equipped with electrical source and photodiode as a detecting unit.

List of Figure

Figure S1. Space charge limited current (SCLC) mobility of 4DBF-BNCZ and 4DBF-PCZ

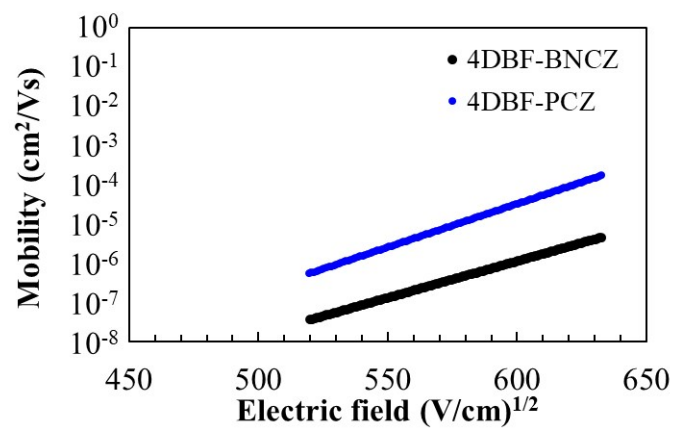


Figure S1.