

Electronic Supplementary Information

Highly Efficient Deep-Blue Emitting Organic Light Emitting Diode Based on the Multifunctional Fluorescent Molecule Comprising Covalently Bonded Carbazole and Anthracene Moieties

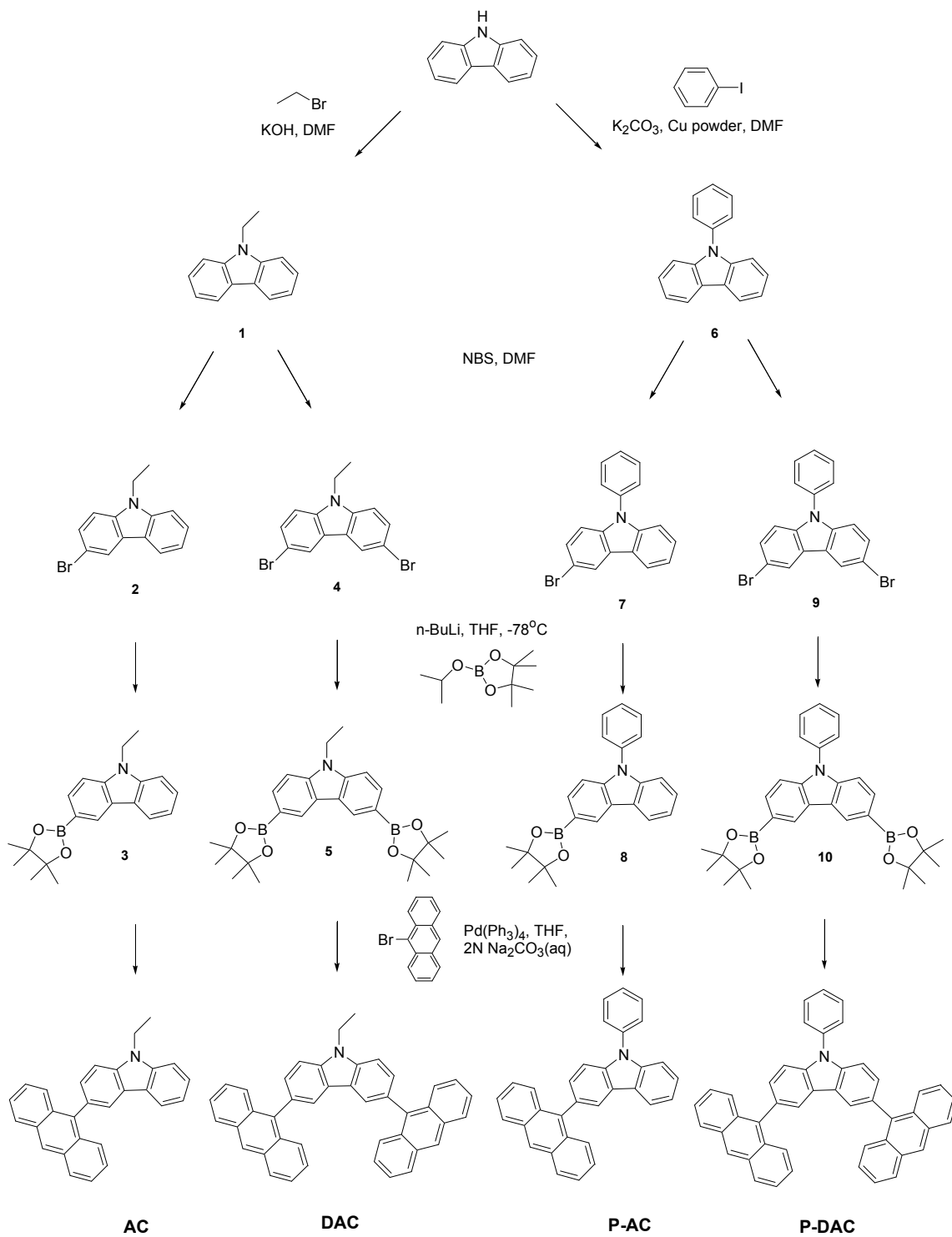
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1. Synthesis of deep-blue emitting molecules



Scheme S1 Synthetic routes to AC, DAC, P-AC, and P-DAC.

Synthesis of 9-ethyl-9H-carbazole (1).

Carbazole (20 g, 119.6 mmol), potassium hydroxide (20.13 g, 358.8 mmol) and bromoethane (39.1 g, 358.8 mmol) were dissolved in DMF (200 ml). The mixture was stirred during overnight at 60 °C. After pouring into brine, and washing, the mixture was extracted by MC. The organic extracts were dried with MgSO₄ and concentrated by rotary evaporation. Purification of solid residue by recrystallization in ethanol gave a white solid (20 g, 102.4 mmol, 85.6%). ¹H NMR (300 MHz, CDCl₃, δ): 8.08 - 8.12 (d, *J* = 7.7 Hz, 2H), 7.44 - 7.50 (t, *J* = 7.5 Hz, 2H), 7.39 - 7.42 (d, *J* = 8.1 Hz, 2H), 7.19 - 7.25 (t, *J* = 6.5 Hz, 2H), 4.34 - 4.42 (q, *J* = 7.2 Hz, 2H), 1.40 - 1.47 (t, *J* = 7.2 Hz, 3H).

Synthesis of 9-phenyl-9H-carbazole (6).

Carbazole (10 g, 59.8 mmol), iodobenzene (12.445 g, 61mmol), copper powder (11.628 g, 183 mmol), and potassium carbonate (25.293 g, 193 mmol) were dissolved in DMF (120 ml) and stirred during overnight at 140 °C under nitrogen atmosphere. After finished the reaction, the reaction mixture was poured into the brine, and washing, the mixture extracted by MC. The organic extracts dried with MgSO₄ and concentrated by rotary evaporation. Purification of solid residue by column chromatography (EA : n-hexane = 1 : 10) gave product (8.1 g, 33 mmol, 56%). ¹H NMR (300 MHz, CDCl₃, δ): 8.12 (d, *J* = 7.8 Hz, 2H), 7.54 - 7.64 (m, 4H), 7.37 - 7.50 (m, 5H), 7.26 - 7.32 (m, 2H).

Synthesis of 3-bromo-9-ethyl-9H-carbazole (2).

To solution of 9-ethyl-9H-carbazole (6 g, 30.7 mmol) in DMF (80 mL), NBS (5.47 g, 30.7 mmol) was added slowly. The mixture was stirred during overnight at room temperature. After pouring into brine, and washing, the mixture was extracted with MC. The organic extracts were dried with MgSO₄ and concentrated by rotary evaporation. Purification of solid residue by reprecipitation with methanol and THF gave white powder (7.16 g, 26.1 mmol, 85%). ¹H NMR (300 MHz, CDCl₃, δ): 8.2 (s, 1H), 8.02 - 8.07 (d, *J* = 8.1 Hz, 1H), 7.52 - 7.56 (d, *J* = 8.7 Hz, 1H), 7.46 - 7.52 (t, *J* = 7.2 Hz, 1H), 7.38 - 7.44 (d, *J*

= 8.1 Hz, 1H), 7.27 - 7.31 (d, $J = 8.7$ Hz, 1H), 7.21 - 7.27 (t, $J = 6.9$ Hz, 1H), 4.28 - 4.39 (q, $J = 7.2$ Hz, 2H), 1.40 - 1.47 (t, $J = 7.2$ Hz, 3H).

Synthesis of 3,6-dibromo-9-ethyl-9H-carbazole (4).

To solution of 9-ethyl-9H-carbazole (7 g, 35.85 mmol) in DMF (150 mL), NBS (13.08 g, 73.5 mmol) was added slowly. The mixture was stirred during overnight at room temperature. After pouring into brine, and washing, the mixture was extracted with MC. The organic extracts were dried with MgSO_4 and concentrated by rotary evaporation. Purification of solid residue by reprecipitation with methanol and THF gave white powder (8.6 g, 24.4 mmol, 68%). ^1H NMR (300 MHz, CDCl_3 , δ): 8.12 - 8.13 (s, 2H), 7.53 - 7.57 (d, $J = 8.7$ Hz, 2H), 7.25 - 7.28 (d, $J = 8.7$ Hz, 2H), 4.25 - 4.35 (q, $J = 7.2$ Hz, 2H), 1.37 - 1.42 (t, $J = 7.2$ Hz, 3H).

Synthesis of 3-bromo-9-phenyl-9H-carbazole (7).

Same procedure with synthesis of 3-bromo-9-ethyl-9H-carbazole (2) was applied with 9-phenyl-9H-carbazole (5g, 20.55 mmol). Product as white powder (5.29g, 16.44 mmol 80%) gained. ^1H NMR (300 MHz, CDCl_3 , δ): 8.24 (s, 1H), 8.09 - 8.06 (d, $J = 7.7$ Hz, 1H), 7.59 - 7.57 (d, $J = 7.4$ Hz, 2H), 7.52 - 7.45 (m, 4H), 7.42 - 7.36 (m, 2H), 7.31 - 7.28 (d, $J = 7.7$ Hz, 1H) , 7.27 - 7.24 (d, $J = 8.8$ Hz, 1H)

Synthesis of 3,6-dibromo-9-phenyl-9H-carbazole (9).

Same procedure with synthesis of 3,6-dibromo-9-ethyl-9H-carbazole (4) was applied with 9-phenyl-9H-carbazole (3.44 g, 14.13 mmol). Product as white powder (5.36 g, 13.36 mmol, 95%) gained. ^1H NMR (300 MHz, CDCl_3 , δ): 8.2 (s, 2H), 7.58 - 7.64 (d, $J = 7.5$ Hz, 2H), 7.48 - 7.53 (m, 5H), 7.23 - 7.26 (d, $J = 7.5$ Hz, 2H).

Synthesis of 9-ethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (3).

To a solution of 3-bromo-9-ethyl-9H-carbazole (2.5 g, 9.12 mmol) in anhydrous THF (100 mL) at -78 °C, 8.53 ml (13.68 mmol) of *n*-butyllithium (1.6 M in hexane) was added. The mixture was stirred at -78 °C for 2 h. 3.72 ml (18.2 mmol) of 2-isopropoxy-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane was added

rapidly to the solution, and the resulting mixture was warmed to room temperature and stirred during overnight. The mixture was poured into water and extracted with MC. The organic extracts were washed with brine and dried with MgSO₄. The solvent was removed by rotary evaporation, and reprecipitation with methanol and THF gave product (1.48 g, 4.51 mmol, 51 %). ¹H NMR (300 MHz, CDCl₃, δ): 8.6 (s, 1H), 8.12 - 8.17 (d, *J* = 7.8 Hz, 1H), 7.9 - 7.96 (d, *J* = 7.8 Hz, 1H), 7.44 - 7.51 (t, *J* = 8.1 Hz, 1H), 7.39 - 7.44 (d, *J* = 8.4 Hz, 1H), 7.21 - 7.28 (t, *J* = 6.6 Hz, 1H), 4.34 - 4.42 (q, *J* = 7.2 Hz, 2H), 1.41 - 1.46 (t, *J* = 7.2 Hz, 3H), 1.40 (s, 12H).

Synthesis of 9-ethyl-3,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (5).

To a solution of 3,6-dibromo-9-ethyl-9H-carbazole (3 g, 8.5 mmol) in anhydrous THF (100 mL) at -78 °C, 15 ml (24 mmol) of *n*-butyllithium (1.6 M in hexane) was added. The mixture was stirred at -78 °C for 2 h. 5.20 ml (25.5 mmol) of 2-isopropoxy-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane was added rapidly to the solution, and the resulting mixture was warmed to room temperature and stirred during overnight. The mixture was poured into water and extracted with MC. The organic extracts were washed with brine and dried with MgSO₄. The solvent was removed by rotary evaporation, and reprecipitation with methanol and THF gave product (2.2g, 5.08 mmol, 60 %). ¹H NMR (300 MHz, CDCl₃, δ): 8.6 (s, 2H), 7.88 - 7.92 (d, *J* = 8.1 Hz, 2H), 7.38 - 7.42 (d, *J* = 8.1 Hz, 2H), 4.34 - 4.42 (q, *J* = 7.2 Hz, 2H), 1.41 - 1.46 (t, *J* = 7.2 Hz, 3H), 1.38 (s, 24H).

Synthesis of 9-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (8).

Same procedure with synthesis of 9-ethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (3) was applied with 3-bromo-9-phenyl-9H-carbazole (3 g, 15.51 mmol). Reprecipitation with methanol and THF gave product (2.57 g, 6.98 mmol, 75%). ¹H NMR (300 MHz, CDCl₃, δ): 8.64 (s, 1H), 8.19 - 8.16 (d, *J* = 7.6 Hz, 1H), 7.87 - 7.84 (d, *J* = 7.3 Hz, 1H), 7.63 - 7.54 (m, 4H), 7.49 - 7.54 (t, *J* = 7.2 Hz, 1H), 7.40 - 7.35 (m, 3H), 7.31 - 7.28 (d, *J* = 7.7 Hz, 1H), 1.40 (s, 12H).

Synthesis of 9-phenyl-3,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (10).

Same procedure with synthesis of 9-ethyl-3,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (5) was applied with 3,6-dibromo-9-phenyl-9H-carbazole (5 g, 12.47 mmol). Recrystallization with methanol and THF gave product (5.15 g, 10.4 mmol, 83%). ¹H NMR (300 MHz, CDCl₃, δ): 8.7 (s, 2H), 7.82 - 7.86 (d, *J* = 8.1 Hz, 2H), 7.45 - 7.62 (m, 5H), 7.34 - 7.38 (d, *J* = 8.1 Hz, 2H), 1.40 (s, 24H).

Synthesis of AC, 3-(anthracen-9-yl)-9-ethyl-9H-carbazole.

9-ethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (1.4 g, 4.36 mmol), 9-bromoanthracene (1.18g, 4.6 mmol) and tetrakis(triphenylphosphine) palladium(0) (0.05 g, 0.044 mmol) were added to a round-bottomed flask equipped with a reflux condenser and dissolved in 45 ml of THF. After adding 15 ml of aqueous 2N sodium carbonate solution, the reaction mixture was heated at 80 °C for 24 h. The cooled crude mixture was poured into water and extracted with CH₂Cl₂ and dried with MgSO₄, filtered, and evaporated to yield a crude product. Flash column chromatography using EA : n-hexane (1 : 4) followed by reprecipitation with methanol and THF gave a product (1.2 g, 3.23 mmol, 74%). ¹H NMR (300 MHz, CDCl₃, δ): 8.52 (s, 1H), 8.16 (s, 1H), 8.04 - 8.09 (m, 3H), 7.73 - 7.77 (d, *J* = 9.0 Hz, 2H), 7.59 - 7.63 (d, *J* = 8.1 Hz, 1H), 7.43 - 7.55 (m, 5H), 7.28 - 7.35 (m, 2H), 7.20 - 7.27 (m, 1H), 4.47 - 4.55 (q, *J* = 7.2 Hz, 2H), 1.55 - 1.60 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (500 MHz, CDCl₃, δ): 140.6, 139.6, 138.2, 131.7, 131.1, 129.2, 129.1, 128.5, 127.5, 126.4, 126.1, 125.3, 125.2, 123.3, 123.2, 123.0, 120.7, 119.2, 108.8, 108.4, 37.9, 14.2; GC-MS (FAB+) (m/z): calcd for C₂₈H₂₁N, 371.17; found, 371.17. Anal. calcd for C₂₈H₂₁N: C 90.53, H 5.70, N 3.77; found: C 90.56, H 5.73, N 3.76.

Synthesis of DAC, 3,6-di(anthracen-9-yl)-9-ethyl-9H-carbazole.

9-ethyl-3,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (2 g, 4.47 mmol), 9-bromoanthracene (2.42 g, 9.4 mmol) and tetrakis(triphenylphosphine) palladium(0) (0.093 g, 0.081 mmol) were added to a round-bottomed flask equipped with a reflux condenser and dissolved in 80 mL of THF. After adding 40 ml of aqueous 2N sodium carbonate solution, the reaction mixture was heated at 85 °C for 24h. The cooled crude mixture was poured into water and extracted with MC and dried with

MgSO₄, filtered, and evaporated to yield a crude product. Flash column chromatography using CHCl₃ followed by reprecipitation with methanol and THF gave a product (0.95 g, 1.73 mmol, 60%). ¹H NMR (300 MHz, CDCl₃, δ): 8.48 (s, 2H), 8.12 (s, 2H), 8.01 - 8.07 (d, *J* = 8.4 Hz, 4H), 7.74 - 7.80 (d, *J* = 8.1 Hz, 4H), 7.68 - 7.72 (d, *J* = 8.4 Hz, 2H), 7.55 - 7.59 (d, *J* = 8.1 Hz, 2H), 7.40 - 7.47 (t, *J* = 8.4 Hz, 4H), 7.27 - 7.35 (t, *J* = 6.6 Hz, 4H), 4.60 - 4.68 (q, *J* = 7.2 Hz, 2H), 1.67 - 1.73 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (500 MHz, CDCl₃, δ): 140.0, 138.0, 131.6, 131.1, 129.4, 128.4, 127.4, 126.4, 125.3, 125.2, 123.4, 123.1, 108.7, 38.2, 14.3; GC-MS (FAB+) (m/z): calcd for C₄₂H₂₉N, 547.23; found, 547.23. Anal. calcd for C₄₂H₂₉N: C 92.11, H 5.34, N 2.56; found: C 92.16, H 5.30, N 2.59.

Synthesis of P-AC, 3-(anthracen-9-yl)-9-phenyl-9H-carbazole.

Same procedure with Synthesis of AC, 3-(anthracen-9-yl)-9-ethyl-9H-carbazole was applied with 9-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (2.5 g, 6.77 mmol). Flash column chromatography using CHCl₃ followed by reprecipitation with methanol and THF gave a product (2.04 g, 4.87 mmol, 72%). ¹H NMR (300 MHz, CDCl₃, δ): 8.52 (s, 1H), 8.20 (s, 1H), 8.10 - 8.08 (d, *J* = 6.6 Hz, 1H), 8.08 - 8.05 (d, *J* = 7.9 Hz, 2H), 7.89 - 7.75 (d, *J* = 8.7 Hz, 2H), 7.72 - 7.63 (m, 4H), 7.62 - 7.59 (d, *J* = 8.4 Hz, 1H), 7.53 - 7.42 (m, 6H), 7.35 - 7.28 (m, 3H); ¹³C NMR (500 MHz, CDCl₃, δ): 141.6, 140.6, 138.0, 131.7, 131.1, 130.4, 130.1, 129.4, 128.5, 127.8, 127.4, 127.4, 126.5, 126.4, 125.4, 125.2, 123.7, 123.5, 123.2, 120.6, 120.3, 110.2, 109.8; GC-MS (FAB+) (m/z): calcd for C₃₂H₂₁N, 419.17; found, 419.17. Anal. calcd for C₃₂H₂₁N: C 91.61, H 5.05, N 3.34; found: C 91.55, H 5.02, N 3.32.

Synthesis of P-DAC, 3,6-di(anthracen-9-yl)-9-phenyl-9H-carbazole.

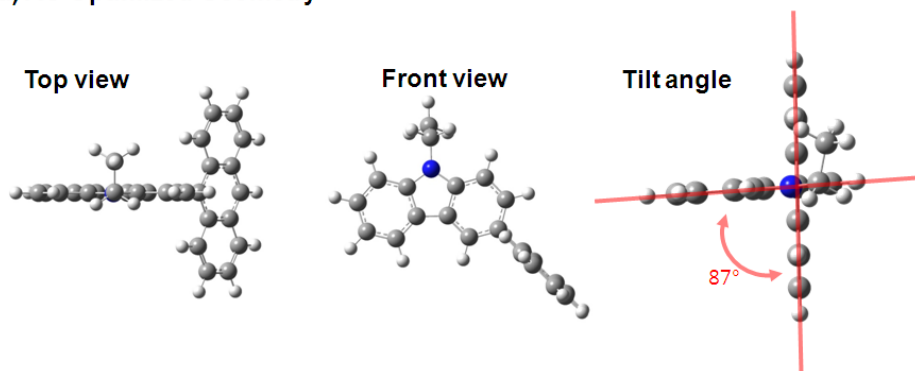
Same procedure with Synthesis of DAC, 3,6-di(anthracen-9-yl)-9-ethyl-9H-carbazole was applied with 9-phenyl-3,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (5.15 g, 10.4 mmol). Flash column chromatography using CHCl₃ followed by reprecipitation with methanol and THF gave a product (3.7 g, 6.21 mmol, 60%). ¹H NMR (300 MHz, CDCl₃, δ): 8.48 (s, 2H), 8.17 (s, 2H), 8.02 - 8.06 (d, *J* = 8.4 Hz, 4H), 7.83 - 7.87 (d, *J* = 8.1 Hz, 2H), 7.76 - 7.80 (d, *J* = 8.4 Hz, 4H), 7.69 - 7.76 (t, *J* = 8.1 Hz, 2H),

7.67 - 7.72 (d, $J = 8.4$ Hz, 2H), 7.55 - 7.62 (t, $J = 7.5$ Hz, 1H), 4.48 - 4.53 (d, $J = 8.4$ Hz, 2H), 7.40 - 7.47 (t, $J = 8.1$ Hz, 4H), 7.29 - 7.36 (t, $J = 8.1$ Hz, 4H); ^{13}C NMR (500 MHz, CDCl_3 , δ): 131.6, 131.0, 130.3, 129.8, 128.5, 127.9, 127.4, 127.3, 126.5, 125.4, 125.2, 123.3, 110.0; GC-MS (FAB+) (m/z): calcd for $\text{C}_{46}\text{H}_{29}\text{N}$, 595.23; found, 595.23. Anal. calcd for $\text{C}_{46}\text{H}_{29}\text{N}$: C 92.74, H 4.91, N 2.35; found: C 92.58, H 4.93, N 2.32.

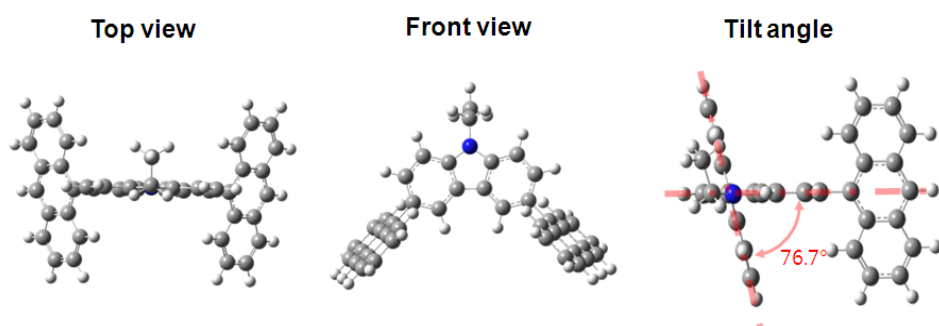
2. Characteristics of deep-blue emitting molecules

To investigate the thermal, electrochemical, and morphological stability of new deep-blue emitting molecules (AC, DAC, P-AC and P-DAC) which comprise carbzole and anthracene moieties, we have studied the characteristics of optimized geometries, orbital energy, and electron densities of the HOMO and LUMO states by theoretical molecular orbital calculation, thermal properties by TGA and DSC, photophysical properties by absorption and PL spectrum, electrochemical properties by repeated cyclic voltammograms, and morphological properties by SEM image.

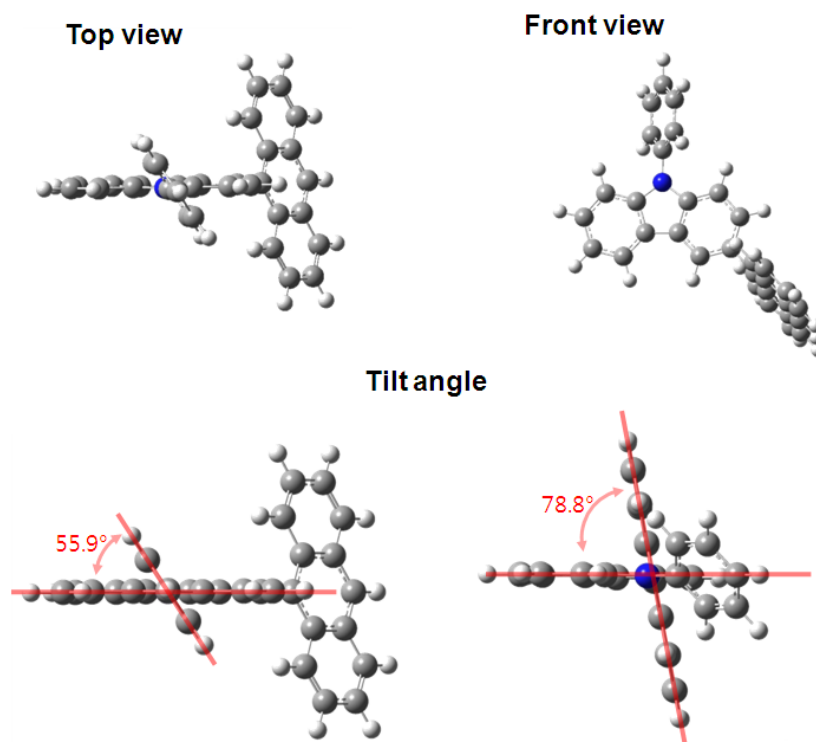
(a) AC Optimized Geometry



(b) DAC Optimized Geometry

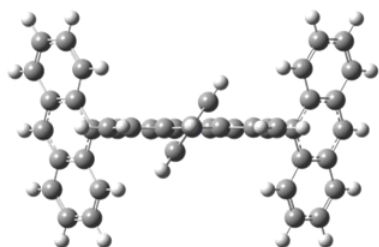


(c) P-AC Optimized Geometry

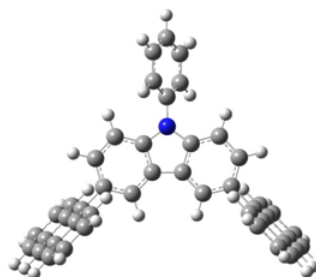


(d) P-DAC Optimized Geometry

Top view



Front view



Tilt angle

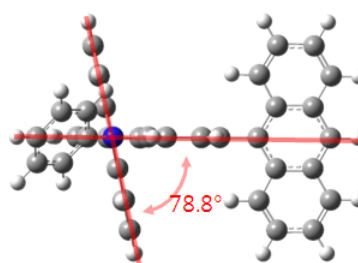
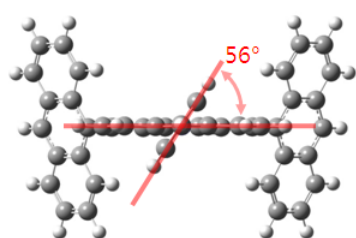


Fig. S1 Three-dimensional optimized geometry of (a) AC, (b) DAC, (c) P-AC, and (d) P-DAC.

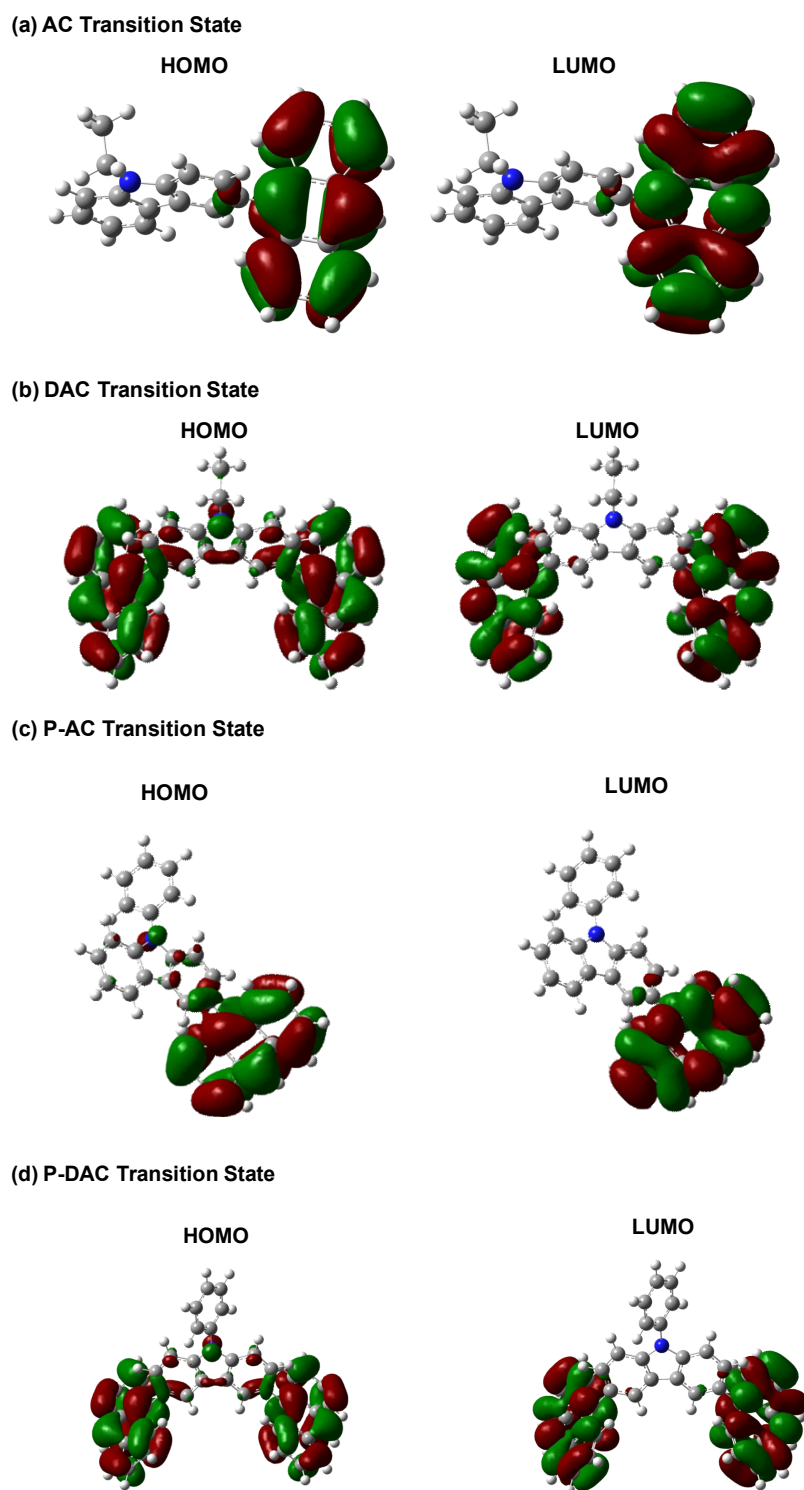


Fig. S2 The calculated HOMO and LUMO electron density maps of (a) AC, (b) DAC, (c) P-AC, and (d) P-DAC.

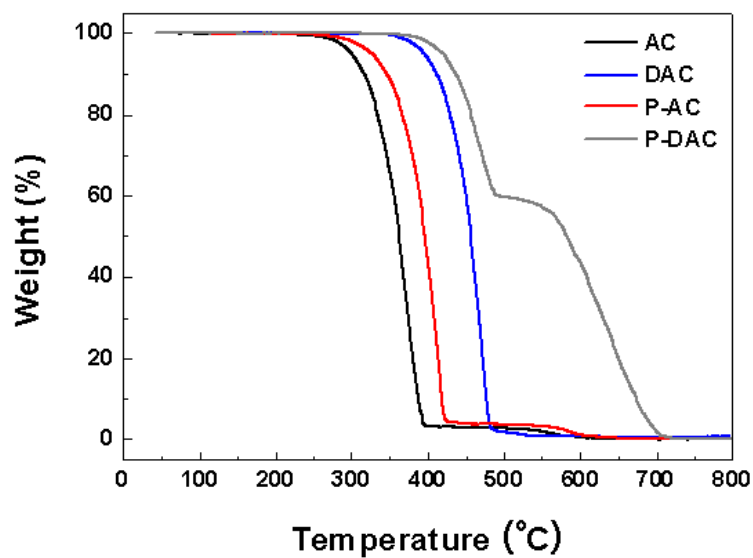


Fig. S3 TGA trace of AC, DAC, P-AC, and P-DAC measured at a scan rate of $10\text{ }^{\circ}\text{C min}^{-1}$ under N_2 .

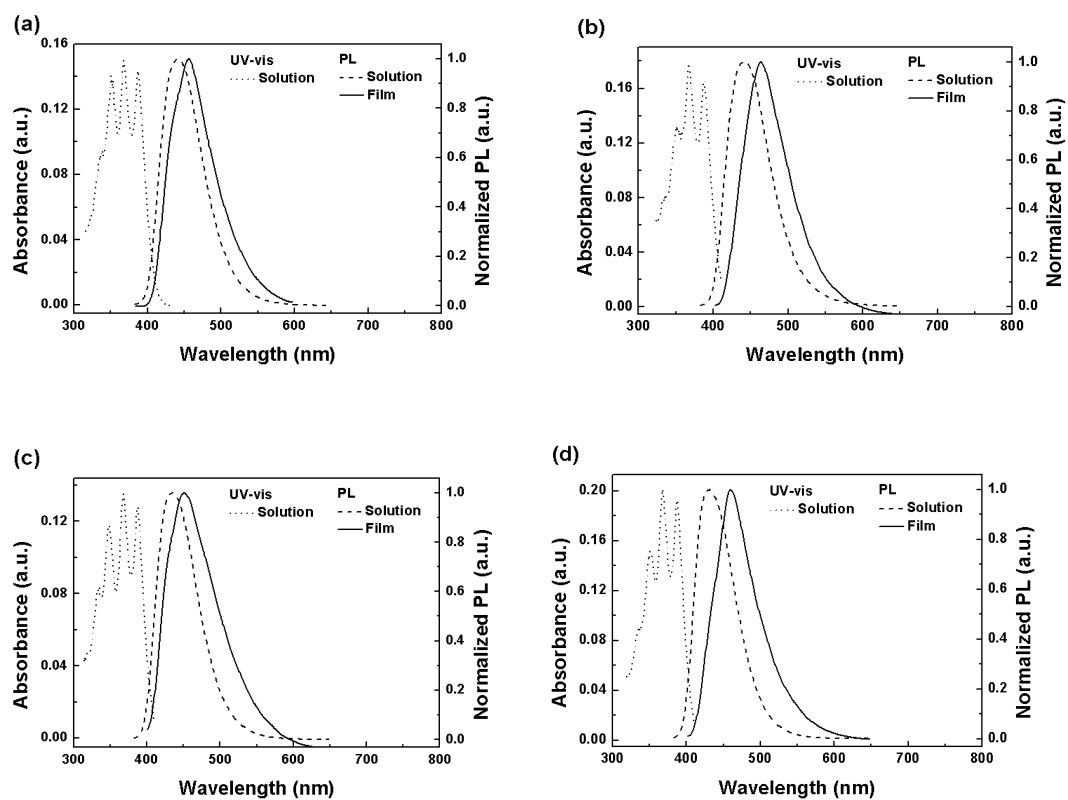


Fig. S4 Absorption and PL spectrum of (a) AC, (b) DAC, (c) P-AC, and (d) P-DAC.

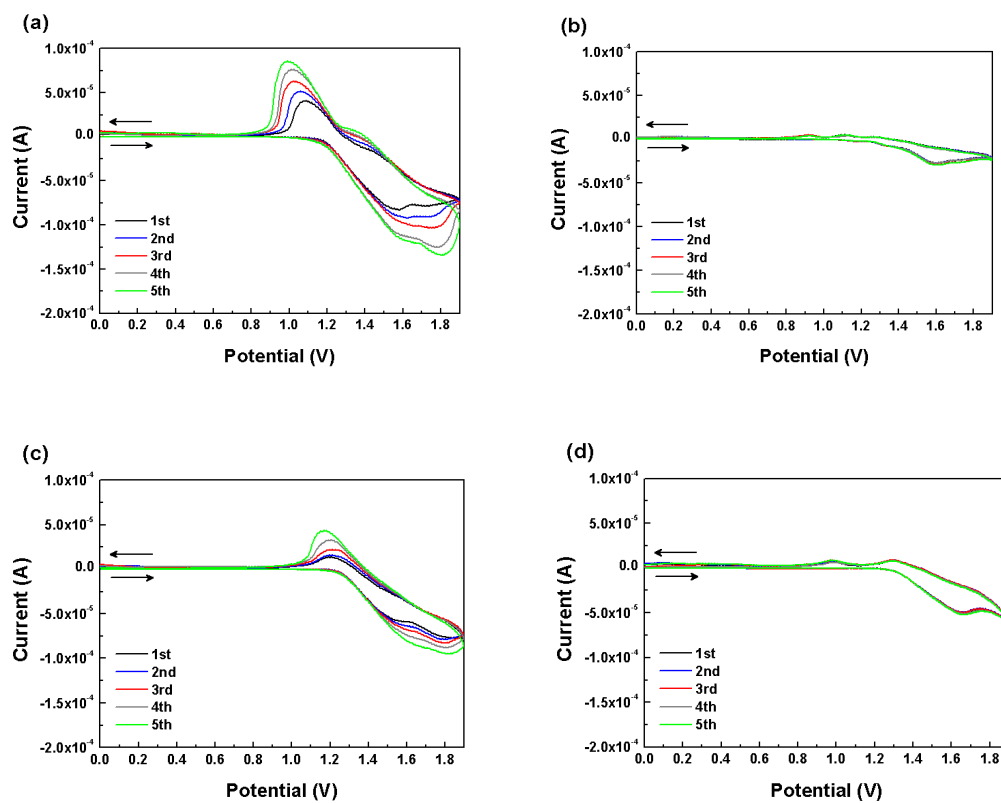


Fig. S5 Repeated cyclic voltammograms of (a) AC, (b) DAC, (c) P-AC, and (d) P-DAC.

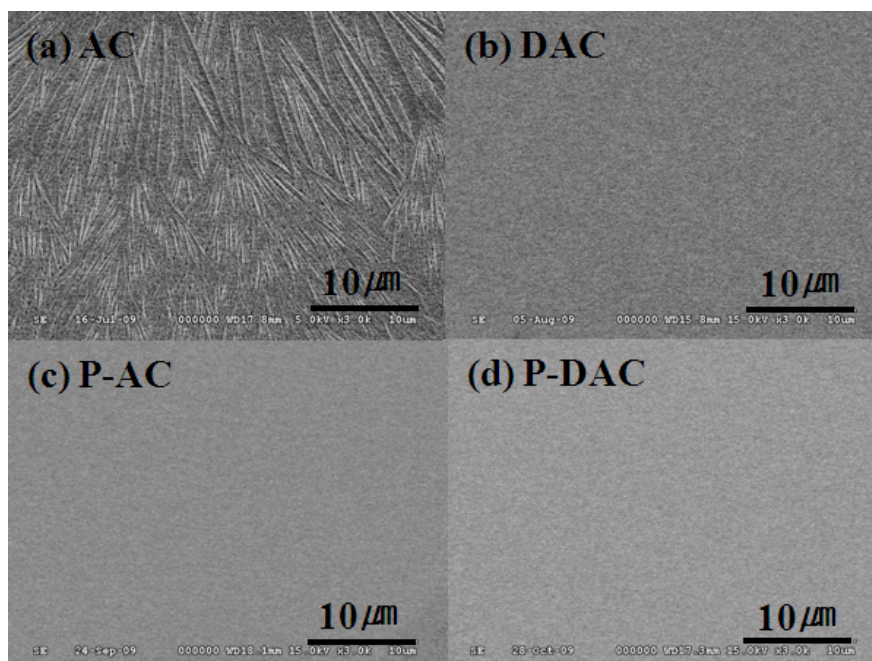


Fig. S6 SEM images of (a) AC, (b) DAC, (c) P-AC, and (d) P-DAC in vacuum deposited film on Si wafer.

The scale bar represents 10 μm and image is magnified by a factor of 3,000.

3. Charge carrier properties of P-DAC

In order to clearly understand the factors affecting device performances of OLEDs using P-DAC as host material, the charge carrier properties of P-DAC were investigated using hole-only device (HOD) and electron-only device (EOD) with the structures of indium tin oxide (ITO) (150nm)/N, N'-bis (naphthalen-1-yl)-N,N'-bis(phenyl)-benzidine (NPB) (50nm)/P-DAC (50nm)/Al (100nm) and ITO (150nm)/Al (100nm)/LiF (1nm)/P-DAC (50nm)/4,7-diphenyl-1,10-phenanthroline (Bphen) (50nm)/LiF (1nm)/Al (100nm). Fig. S7 shows the current density-voltage (J-V) characteristics of these devices and molecular structures of NPB and Bphen. P-DAC shows well-balanced charge carrier properties, although the hole current is relatively higher than electron current by excellent hole transporting ability of carbazole moiety.

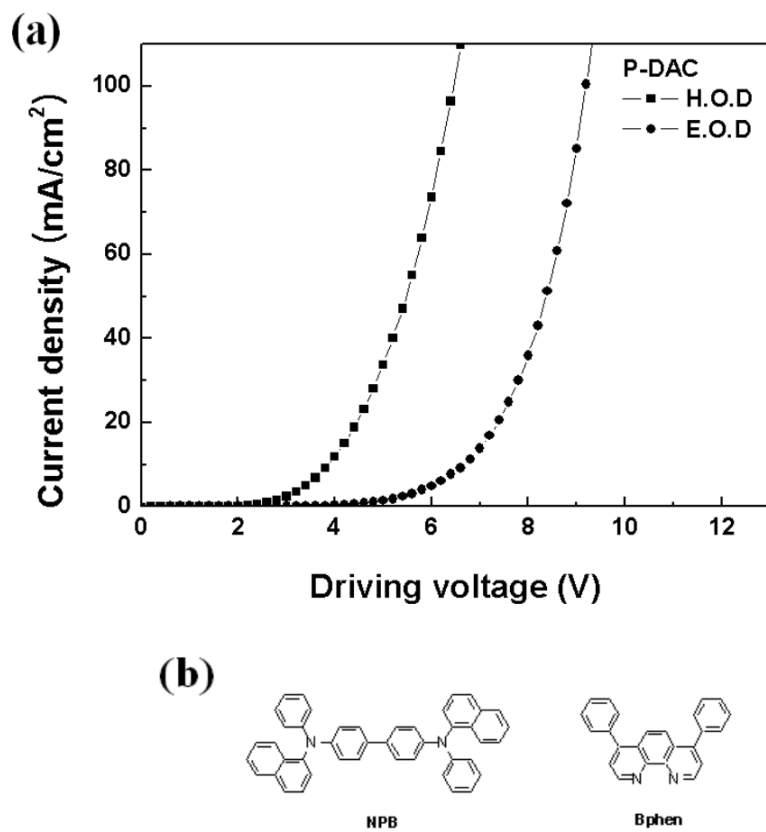


Fig. S7 (a) J-V characteristics of HOD and EOD with P-DAC. (b) Molecular structures of NPB and Bphen.