Supporting information

Solution Processable Polyphenylphenyl Dendron Bearing Molecules for Highly Efficient Blue Light-Emitting Diodes

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Synthesis and characterization of the four blue light emitting materials

2-(Trimethylsilyl)ethynyl-5-bromopyridine (2A)

To a solution of 2,5-dibromopyridine (3.56 g, 0.015 mol), CuI (0.07 g, 0.37 mmol), and Pd(PPh₃)₂Cl₂ (0.26 g, 0.37 mmol) in 100 ml of diisopropylamine was added (trimethylsilyl)acetylene (1.47 g, 0.015 mol). The mixture was stirred at room temperature overnight under nitrogen atmosphere. After removal of the solvent under reduce pressure, the residue was purified by flash column to offer 3.45 g (yield 90%) of 2-(trimethylsilyl)ethynyl-5-bromopyridine. MS: *m/z* 252.8 (47%), 254.8 (47%). ¹H NMR (ppm) (400 MHz, CDCl₃) δ 8.640 (s, 1 H), 7.801 (d, 1 H, J = 8.0 Hz), 7.368 (d, 1 H, J = 8.0 Hz), 0.289 (s, 9 H)

1-(Trimethylsilyl)ethynyl-4-bromobenzene (2B)

To a solution of 1,4-dibromobenzene (3.56 g, 0.015 mol), CuI (0.07 g, 0.37 mmol), and Pd(PPh₃)₂Cl₂ (0.26 g, 0.37 mmol) in 100 ml of diisopropylamine was added

(trimethylsilyl)acetylene (1.47 g, 0.015 mol). The mixture was stirred at room temperature overnight under nitrogen atmosphere. After removal of the solvent under reduce pressure, the residue was purified by column chromatography eluted with Hexane to offer 2.07 g (yield 54%) of 1-(trimethylsilyl)ethynyl-4-bromobenzene. m/z 251.8 (38%), 253.8 (40%). ^1H NMR (ppm) (400 MHz, CDCl_3) δ 7.463 (d, 2 H, $J = 8.0$ Hz), 7.350 (d, 2 H, $J = 8.0$ Hz), 0.267 (s, 9H).

2-(Trimethylsilyl)ethynyl-5-bromothiophene (2C)

To a solution of 2,5-dibromothiophene (3.66 g, 0.015 mol), CuI (0.07 g, 0.37 mmol), and $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.26 g, 0.37 mmol) in 100 ml of diisopropylamine was added (trimethylsilyl)acetylene (1.47 g, 0.015 mol). The mixture was stirred at room temperature overnight under nitrogen atmosphere. After removal of the solvent under reduce pressure, the residue was purified by column with Hexane as the mobile-phase to offer 1.63 g (yield 42%) of 2-(trimethylsilyl)ethynyl-5-bromothiophene. m/z 257.8 (35%), 259.8 (40%). ^1H NMR (ppm) (400 MHz, CDCl_3) δ 6.992 (d, 1 H, $J = 4.0$ Hz), 6.926 (d, 1 H, $J = 4.0$ Hz), 0.260 (s, 9H).

1-(Trimethylsilyl)ethynyl-2,5-dimethoxy-4-bromobenzene (2D)

To a solution of 2,5-dimethoxy-1,4-dibromobenzene (4.44 g, 0.015 mol), CuI (0.07 g, 0.37 mmol), and $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.26 g, 0.37 mmol) in the mixture of 30 ml of diisopropylamine and 100 ml toluene was added (trimethylsilyl)acetylene (1.47 g, 0.015 mol). The mixture was stirred at room temperature overnight under nitrogen atmosphere. After removal of the solvent

under reduce pressure, the residue was purified by column with the mixture of Hexane and CH_2Cl_2 (8:1) as the mobile-phase to offer 2.39 g (yield 51%) of 1-(trimethylsilyl)ethynyl-2,5-dimethoxy-4-bromobenzene. m/z 313.9 (100%), 313.9 (100%). ^1H NMR (ppm) (400 MHz, CDCl_3) δ 7.082 (s, 1 H), 6.986(s, 1 H), 3.871 (s, 3 H), 3.857 (s, 3 H), 0.291 (s, 9 H).

2-(2',3',4',5'-Tetraphenyl)phenyl-5-bromopyridine (3A)

To a solution of 2-(trimethylsilyl)ethynyl-5-bromopyridine (1.27 g, 5 mmol) in the mixture of THF and methanol was added 1ml of NaOH (5 N). The reaction mixture was stirred for 1 hour at room temperature and then 50 ml of ethyl acetate was added. The mixture was washed with water and brine and dried with anhydrous magnesium sulfate. After removal of the solvent, the residue was refluxed with tetraphenylcyclopentadienone (2 g, 5.2 mmol) in 50 ml o-xylene overnight. After cooled down to room temperature, the solvent was removed by flash column and the residue was purified through recrystallization in ethanol to offer 2.17 g (yield 81%) of pure 2-(2',3',4',5'-tetraphenyl)phenyl-5-bromopyridine. m/z 537.9 (100%), 535.8 (47%). ^1H NMR (ppm) (400 MHz, CDCl_3) δ 8.659 (d, 1 H, $J = 2$ Hz), 7.803(s, 1 H), 7.490 (dd,1 H), 7.165 (s, 5 H), 7.017-6.769 (m, 16 H).

1-(2',3',4',5'-Tetraphenyl)phenyl-4-bromo-benzene (3B)

To a solution of 1-(trimethylsilyl)ethynyl-4-bromobenzene (1.27 g, 5 mmol) in the mixture of THF and methanol was added 1ml of NaOH (5 N). The reaction mixture was stirred for 1 hour at room temperature and then 50 ml of ethyl acetate was added. The mixture was washed with

water and brine and dried with anhydrous magnesium sulfate. After removal of the solvent, the residue was refluxed with tetraphenylcyclopentadienone (2 g, 5.2 mmol) in 50 ml o-xylene overnight. After cooled down to room temperature, the solvent was removed by flash column and the residue was purified through recrystallization in ethanol to offer 2.40 g (yield 90%) of pure 1-(2',3',4',5'-tetraphenyl)phenyl-4-bromobenzene. m/z 537.8 (100%), 535.8 (100%). ^1H NMR (ppm) (400 MHz, CDCl_3) δ 7.540 (s, 1 H), 7.321(d, 2 H, $J = 8$ Hz), 7.180 (s, 5 H), 7.061 (d, 2 H, $J = 8$ Hz), 6.988-6.788 (m, 15 H).

2-(2',3',4',5'-Tetraphenyl)phenyl-5-bromo-thiophene (3C)

To a solution of 2-(trimethylsilyl)ethynyl-5-bromothiophene (1.30 g, 5 mmol) in the mixture of THF and methanol was added 1ml of NaOH (5 N). The reaction mixture was stirred for 1 hour at room temperature and then 50 ml of ethyl acetate was added. The mixture was washed with water and brine and dried with anhydrous magnesium sulfate. After removal of the solvent, the residue was refluxed with tetraphenylcyclopentadienone (2 g, 5.2 mmol) in 50 ml o-xylene overnight. After cooled down to room temperature, the solvent was removed by flash column and the residue was purified by column to offer 1.74 g (yield 64%) of pure 2-(2',3',4',5'-tetraphenyl)phenyl-5-bromothiophene. m/z 543.7 (99%), 541.7 (99%). ^1H NMR (ppm) (400 MHz, CDCl_3) δ 7.671 (s, 1 H), 7.191 (d, 5 H), 7.110 (t, 3 H) 7.015 (m, 2 H), 6.937 (m, 3 H), 6.850-6.782 (m, 8 H), 6.492 (d, 1 H, $J = 4$ Hz).

1-(2',3',4',5'-Tetraphenyl)phenyl-2,5-dimethoxy-4-bromo-benzene (3D)

To a solution of 1-(trimethylsilyl)ethynyl-2,5-dimethoxy-4-bromobenzene (1.56 g, 5 mmol) in the mixture of THF and methanol was added 1 ml of NaOH (5 N). The reaction mixture was stirred for 1 hour at room temperature and then 50 ml of ethyl acetate was added. The mixture

was washed with water and brine and dried with anhydrous magnesium sulfate. After removal of the solvent, the residue was refluxed with tetraphenylcyclopentadienone (2 g, 5.2 mmol) in 50 ml o-xylene overnight. After cooled down to room temperature, the solvent was removed by flash column to offer 2.6 g of a mixture of 1-(2',3',4',5'-terraphenyl)phenyl-2,5-dimethoxy-4-bromobenzene and tetraphenylcyclopentadienone. The crude product was used for the next reaction without further purification.

2-(2',3',4',5'-Tetraphenyl)phenyl-5-(*p*-N,N-dimethyl)phenyl-pyridine (Blue A)

In an argon flushed two-neck round-bottom flask, a mixture of 0.80 g (1.5 mmol) of 2-(2',3',4',5'-tetraphenyl)phenyl-5-bromopyridine, 36 mg of tetrakis(triphenylphosphine)palladium(0), 0.66 g (4 mmol) of *p*-N,N,-dimethylphenylboronic acid, 10 ml of 2 M sodium carbonate and 25 ml of toluene was added and heated at reflux for four hours. After cooling down, the reaction mixture was extracted with ethyl acetate and the organic phase was washed with brine and dried over magnesium sulfate. After the solvent was removed on a rotary evaporator, the residue was purified by flash column eluted with hexane/CH₂Cl₂ (3:1) to provide 0.83 g of **Blue A** (yield 96%). MS: *m/z* 578.8 (100%). ¹H NMR (ppm) (400 MHz, CDCl₃) δ 8.823 (s, 1 H), 7.890 (s, 1 H), 7.535-7.481 (m, 2 H), 7.186-6.800 (m, 24 H), 3.019 (s, 6 H). ¹³C NMR (ppm) (400 MHz, CDCl₃) 146.3, 141.2, 141.1, 140.2, 139.1, 132.4, 131.5, 131.4, 131.3, 131.2, 130.0, 127.5, 127.4, 127.1, 126.8, 126.5, 126.1, 125.8, 125.5, 125.3, 125.1, 112.8, 40.4. Anal. Calcd for C₄₃H₃₄N₂: C, 89.24; H, 5.92. Found: C, 88.70; H, 5.73.

1-(2',3',4',5'-Tetraphenyl)phenyl-4-(*p*-N,N-dimethyl)phenyl-benzene (Blue B)

In an argon flushed two-neck round-bottom flask, a mixture of 0.80 g (1.5 mmol) of 1-(2',3',4',5'-tetraphenyl)phenyl-4-bromobenzene, 36 mg of tetrakis(triphenylphosphine)palladium(0), 0.66 g (4 mmol) of p-N,N,-dimethylphenylboronic acid, 10 ml of 2 M sodium carbonate and 25 ml of toluene was added and heated at reflux for four hours. After cooling down, the reaction mixture was extracted with ethyl acetate and the organic phase was washed with brine and dried over magnesium sulfate. After the solvent was removed on a rotary evaporator, the residue was purified by column eluted with hexane/CH₂Cl₂ (8:1) to provide 0.80 g of **Blue B** (yield 93%). MS: *m/z* 577.9 (100%). ¹H NMR (ppm) (400 MHz, CDCl₃) δ 7.640 (s, 1 H), 7.510 (d, 2 H, J = 8.0 Hz), 7.401 (d, 2 H, J = 8.0 Hz), 7.189-6.822 (m, 24 H), 3.007 (s, 6 H). ¹³C NMR (ppm) (400 MHz, CDCl₃) 139.8, 139.2, 131.4 130.4, 130.0, 127.6, 127.0, 126.9, 126.6, 126.0, 125.6, 125.3. Anal. Calcd for C₄₄H₃₅N: C, 91.47; H, 6.11. Found: C, 91.29; H, 5.94.

2-(2',3',4',5'-Tetraphenyl)phenyl-5-(p-N,N-dimethyl)phenyl-thiophene (Blue C)

In an argon flushed two-neck round-bottom flask, a mixture of 0.81 g (1.5 mmol) of 2-(2',3',4',5'-tetraphenyl)phenyl-5-bromothiophene, 36 mg of tetrakis(triphenylphosphine)palladium(0), 0.66 g (4 mmol) of p-N,N,-dimethylphenylboronic acid, 10 ml of 2 M sodium carbonate and 25 ml of toluene was added and heated at reflux for four hours. After cooling down, the reaction mixture was extracted with ethyl acetate and the organic phase was washed with brine and dried over magnesium sulfate. After the solvent was removed on a rotary evaporator, the residue was purified by column eluted with hexane/CH₂Cl₂ (8:1) to provide 0.36 g of **Blue C** (yield 41%). MS: *m/z* 583.8 (100%). ¹H NMR (ppm) (400 MHz, CDCl₃) δ 7.786 (s, 1 H), 7.402 (d, 2 H, J = 8.0 Hz), 7.203 (s, 5 H),

7.083-7.067 (d, 5 H), 6.931-6.526 (m, 14 H), 2.986 (s, 6 H). ^{13}C NMR (ppm) (400 MHz, CDCl_3) 131.4, 131.2, 129.8, 128.1, 127.6, 127.4, 126.8, 126.6, 126.4, 125.6, 125.4. Anal. Calcd for $\text{C}_{42}\text{H}_{33}\text{NS}$: C, 86.41; H, 5.70. Found: C, 85.92; H, 5.68.

1-(2',3',4',5'-Tetraphenyl)phenyl-2,5-dimethoxy-4-(*p*-N,N-dimethyl)phenyl-benzene (Blue D)

In an argon flushed two-neck round-bottom flask, a mixture of 1.0 of the crude compound of 1-(2',3',4',5'-tetraphenyl)phenyl-2,5-dimethoxy-4-bromobenzene (containing small amount of tetraphenylcyclopentadienone), 36 mg of tetrakis(triphenylphosphine)palladium(0), 0.66 g (4 mmol) of *p*-N,N-dimethylphenylboronic acid, 10 ml of 2 M sodium carbonate and 25 ml of toluene was added and heated at reflux for four hours. After cooling down, the reaction mixture was extracted with ethyl acetate and the organic phase was washed with brine and dried over magnesium sulfate. After the solvent was removed on a rotary evaporator, the residue was purified by column eluted with hexane/ CH_2Cl_2 (6:1) to provide 0.81 g of pure **Blue D** (yield ~90%). MS: m/z 637.7 (100%). ^1H NMR (ppm) (400 MHz, CDCl_3) δ 7.860 (s, 1 H), 7.473 (d, 2 H, $J = 8.0$ Hz), 7.195 (s, 5 H), 6.947-6.695 (m, 19 H), 3.602 (s, 3 H), 3.479 (s, 3 H), 3.008 (s, 6 H). ^{13}C NMR (ppm) (400 MHz, CDCl_3) 141.8, 141.3, 140.4, 140.1, 131.6, 131.1, 130.5, 130.0, 127.5, 126.9, 126.5, 126.1, 125.5, 125.2, 116.2, 112.3, 56.2, 55.6. Anal. Calcd for $\text{C}_{46}\text{H}_{39}\text{NO}_2$: C, 86.82; H, 6.16. Found: C, 86.37; H, 6.39.

Fig. 1 UV-absorption of the materials in CHCl_3

Fig. 2 Photo luminance of the materials in CHCl_3

Fig. 3 Electrochemical behaviors of the materials in 0.10 M of tetrabutylammonium perfluorate phosphate (Bu_4NPF_6) in anhydrous CH_2Cl_2 solution.