Supporting information for "Synthesis and optical properties of amino-functionalized azaborines and ladder-type azaborines"

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Contents

1. Synthesis of the compounds

General remarks: General chemicals were used as received. Cyclohexane for fluorometric grade (Dojindo) was used for optical measurement. All manipulations were carried out using Schlenk technique under an argon atmosphere. Solvents were purified by MBRAUN MB-SPS system. Wet column chromatography (WCC) was performed using Kanto Silica Gel 60N. Gel permeation liquid chromatography (GPLC) was performed using LC-918 or LC-908 with JAIGEL 1H+2H columns (Japan Analytical Industry) using chloroform or toluene as solvents, respectively. NMR spectra were recorded by a JEOL AL-400 spectrometer (^{1}H, 400 MHz; ^{13}C, 100 MHz; ^{11}B, 128 MHz) or a Bruker DRX-500 spectrometer (^{1}H, 500 MHz; ^{13}C, 126 MHz). Chemical shifts are reported in δ. ^{1}H NMR spectra are referenced to residual protons in deuterated solvent; ^{13}C NMR spectra are referenced to carbon-13 in the deuterated solvent; ^{11}B NMR spectra are referenced to an external standard of $BF_3 \bullet Et_2O$. Low resolution mass spectra were obtained with a JEOL JMS-700P using *m*-nitrobenzylalchol as a matrix. High resolution mass spectra were recorded by a JEOL JMS-700P using PEG600 or Ultramark® as internal standards. UV-vis spectra were recorded on a JASCO V-530 spectrophotometer. Fluorescence spectra were recorded on a JASCO FP-6500 fluorescence spectrophotometer. All melting points were measured with a Yanaco MP-S3 and uncorrected. Elemental analyses were performed by the Microanalytical Laboratory of Department of Chemistry, Faculty of Science, The University of Tokyo. Bis(2,4-dibromophenyl)amine,[1] 2,4-dibromoaniline,[2] 1,4-dibromo-2,5-diiodobenzene[3] and 3,6-di-*t*-butyl-9*H*-carbazole[4] were synthesized according to literatures.

Synthesis of bis(2,4-dibromophenyl)hexylamine (1): A mixture of bis(2,4-dibromophenyl)amine (22 g, 45 mmol), KOH (13 g, 0.23 mol), $Bu^n{}_4NI$ (1.8 g, 5.0 mmol) and THF (300 mL) was refluxed for 1 h. To this mixture was added Hex^nI (6.9 mL, 47 mmol), and the mixture was refluxed for 4 h. The mixture was treated with aqueous NH_4Cl and extracted with Et_2O, and the solvents were removed under reduced pressure. The residual oil was dissolved in Et_2O, and the solution was washed with water. The organic layer was dried over anhydrous Na_2SO_4, and the solvents were removed under reduced pressure. The residual oil was subjected to column chromatography (SiO_2, eluent: hexane) to give **1** as a colorless oil (22 g, 86%). ^1H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, *J* = 6.8 Hz, 3H), 1.27-1.37 (m, 6H), 1.60 (quint, *J* = 6.8 Hz, 2H), 3.49 (t, *J* = 8.0 Hz, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 7.33 (dd, *J* = 8.8, 2.0Hz, 2H), 7.70 (d, *J* = 2.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.07, 22.64, 26.54, 27.64, 31.56, 53,15, 116.61, 121,67, 125.85, 130.79, 136.59, 146.07; HRMS (FAB^+) *m*/*z* calcd for $C_{18}H_{19}{}^{79}Br_2{}^{81}Br_2$ 568.8210, found 568.8203.

Synthesis of 3a: To a Et_2O (10 mL) solution of **1** (0.50 g, 0.88 mmol) was added Bu^nLi (1.2 mL, 1.9 mmol) at –75 °C, and the mixture was stirred at rt for 20 min. To the solution was added $MesB(OMe)_2$ (0.20 mL, 0.97 mmol), and the mixture was stirred at rt for 1 h. The resulting yellow suspension was treated with aqueous NH_4Cl and extracted with Et_2O. The extracts were dried over anhydrous Na_2SO_4, and the solvents were removed under reduced pressure to give pure **3a** as yellow solids (0.47 g, 98%). mp 200-202 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 0.97 (t, *J* = 7.2 Hz, 3H), 1.40-1.52 (m, 4H), 1.62 (quint, *J* = 7.6 Hz, 2H), 1.92 (s, 6H), 2.02 (quint, *J* = 7.6 Hz, 2H), 2.40 (s, 3H), 4.45 (t, *J* = 8.4 Hz, 2H), 6.94 (s, 2H), 7.52 (d, *J* = 9.2 Hz, 2H), 7.81 (dd, *J* = 9.2, 2.4 Hz, 2H), 7.89 (d, *J* = 2.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.09, 21.35, 22.75, 23.33, 26.67, 27.26, 31.59, 48.32, 113.29, 116.88, 127.01, 136.44, 136.73, 139.00, 139.13, 143.76 (Two signals corresponding to the carbon atoms adjacent to the boron atom could not be observed.); HRMS (FAB^+) *m*/*z* calcd for $C_{27}H_{30}{}^{11}B^{79}Br^{81}BrN$ 539.0818, found 539.0845.

Synthesis of 3b: To a Et_2O (100 mL) solution of **1** (5.0 g, 8.8 mmol) was added Bu^nLi (1.6 M hexane solution) (12 mL, 19 mmol) at –75 °C, and the mixture was warmed to rt and stirred for 10 min. To this mixture was added TipB(OMe)$_2$ (2.6 mL, 8.8 mmol), and the mixture was stirred for 1 h at rt. The mixture was treated with aqueous NH_4Cl and extracted with Et_2O. The extracts were dried over anhydrous Na_2SO_4, and the solvents were removed under reduced pressure. The residual yellow solids were recrystallized from $CHCl_3$-EtOH to give **3b** as yellow solids (4.1 g, 75%). mp 221-223 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.95-1.03 (m, 15H), 1.38 (d, *J* = 7.0 Hz, 6H), 1.42-1.47 (m, 4H), 1.60 (quint, *J* = 7.2 Hz, 2H), 2.05 (quint, *J* = 7.6 Hz, 2H), 2.24 (sept, *J* = 6.8 Hz, 2H), 3.00 (sept, *J* = 7.0 Hz, 1H), 4.43 (t, *J* = 8.4 Hz, 2H), 7.07 (s, 2H), 7.49 (d, *J* = 9.0 Hz, 2H), 7.78 (dd, J = 9.0, 2.4 Hz, 2H), 7.95 (d, J = 2.4 Hz, 2H); 13C NMR (126 MHz, CDCl3) d 14.03, 22.69, 24.14, 24.31, 26.61, 27.14, 31.54, 34.24, 35.12, 48.35, 112.97, 116.73, 120.04. 130.17, 136.01, 136.28, 139.75, 143.47, 148.29, 150.40; HRMS (FAB$^+$) *m*/*z* calcd for $C_{33}H_{42}N^{79}Br_2{}^{11}B$ 621.1777, found: 621.1767.

Synthesis of 3c: A mixture of **3b** (0.10 g, 0.16 mmol), Hex^{n}NH$_2$ (60 µl, 0.45 mmol), Bu^{t}ONa (60 mg, 0.62 mmol), Pd(dba)$_2$ (13 mg, 23 µmol), BINAP (14 mg, 23 µmol) and toluene (5 mL) was stirred at 110 °C for 22 h. The mixture was treated with aqueous NH_4Cl and extracted with Et_2O. The extracts were dried over anhydrous Na_2SO_4, and the solvents were removed under reduced pressure. The residue was subjected to GPLC to give **3e** as yellow orange oil (63 mg, 59%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, *J* =6.8 Hz, 6H), 0.95-1.00 (m, 15H), 1.25-1.32 (m, 10H), 1.36 (d, *J* = 6.8 Hz, 6H), 1.40-1.62 (m, 10H), 2.05 (quint, *J* = 7.6 Hz, 2H), 2.45 (quint, *J* = 6.7 Hz, 2H), 3.01 (t, *J* = 7.2 Hz, 4H), 3.33 (brs, 2H), 4.41 (t, *J* = 7.0 Hz, 2H), 6.99 (d, *J* = 2.3 Hz, 2H), 7.13 (dd, *J* = 9.2, 2.3 Hz, 2H), 7.46 (d, *J* = 9.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.11, 14.14, 22.65, 22.81, 24.29, 24.66, 26.84, 27.57, 29.65, 31.68, 34.28, 34.72, 45.21, 47.75, 114.96, 118.85, 119.33, 121.56, 128.66, 138.33, 139.06, 140.16, 147.10, 150.39; HRMS (FAB$^+$) *m*/*z* calcd for $C_{45}H_{70}{}^{11}BN_3$ 663.5662, found: 663.5624.

Synthesis of 3d: A mixture of **3a** (0.50 g, 0.93 mmol), Ph_2NH (0.47 g, 2.8 mmol), Bu^{t}ONa (0.27 g, 2.8 mmol), Pd(OAc)$_2$ (30 mg, 0.13 mmol), DPPF (0.15 g, 0.26 mmol) and toluene (10 mL) was stirred at 105 °C for 10 h to give fluorescence green solution. The solution was treated with aqueous NH_4Cl and extracted with Et_2O. The extracts were dried over anhydrous Na_2SO_4, and the solvents were removed under reduced pressure. The residue was subjected to column chromatography (SiO_2, eluent: $CHCl_3$-hexane 1:3) and GPLC to give **3d** as yellow solids (0.43 g, 65%). mp 168-170 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.95 (t, *J* = 7.0 Hz, 3H), 1.37-1.51 (m, 4H), 1.59 (quint, *J* = 7.6 Hz, 2H), 1.84 (s, 6H), 2.09 (quint, *J* = 8.2 Hz, 2H), 2.21 (s, 3H), 4.46 (brs, 2H), 6.68 (s, 2H), 6.90 (t, *J* = 7.4 Hz, 4H), 7.01 (d, *J* = 7.4 Hz, 8H), 7.16 (t, *J* = 7.4 Hz, 8H); 7.50 (dd, *J* = 9.2 Hz, 2H), 7.56-7.59 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.04, 21.09, 22.71, 23.22, 26.66, 27.34, 31.53, 48.30, 116.02, 121.69, 122.59, 126.76, 127.83, 128.93, 132.58, 133.88, 136.01, 138.90, 142.08, 147.90 (One signal corresponding to the carbon atom adjacent to the boron atom was not observed.); HRMS (FAB$^+$) *m*/*z* calcd for $C_{51}H_{50}N_3{}^{11}B$ 715.4098, found 715.4109.

Synthesis of 3e: A mixture of **3b** (0.10 g, 0.16 mmol), carbazole (70 mg, 0.54 mmol), Bu^{t}ONa (52 mg, 0.54 mmol), $Pd(dba)_2$ (6 mg, 10 μmol), PBu$^t_2$(2-Biph) (4.5 mg, 15 μmol) and toluene (5 mL) was stirred at 120 °C for 16 h. The mixture was treated with aqueous NH_4Cl and extracted with Et_2O. The extracts were dried over anhydrous Na_2SO_4, and the solvents were removed under reduced pressure. The residue was subjected to GPLC to give **3e** as yellow solids (105 mg, 81%). mp 274-276 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.71-1.03 (m, 15H), 1.15 (d, *J* = 6.9 Hz, 6H), 1.50 (sext, *J* = 7.2 Hz, 2H), 1.59 (quint, *J* = 7.4 Hz, 2H), 1.76 (quint, *J* = 7.59 Hz, 2H), 2.31 (sept, *J* = 8.0 Hz, 2H), 2.51 (sext, *J* = 6.2 Hz, 2H), 2.77 (sept, *J* = 6.9 Hz, 1H), 4.70 (t, *J* = 8.4 Hz, 2H), 6.87 (s, 2H), 7.23-7.27 (m, 8H), 7.35 (td, *J* = 7.1, 0.8 Hz, 4H), 7.88-7.93 (m, 4H), 8.11 (d, *J* = 2.3 Hz, 2H), 8.13 (d, *J* =7.6 Hz, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.10, 22.79, 23.92, 24.32, 26.76, 27.46, 31.65, 34.04, 35.10, 109.63, 116.51, 119.56, 119.97, 120.21, 122.93, 125.80, 129.14, 133.23, 136.83, 141.61, 144.29, 148.09, 149.95 (Two signals corresponding to carbon atoms adjacent to the boron atomwere not observed.); HRMS (FAB$^+$) *m*/*z* calcd for $C_{57}H_{58}N_3{}^{11}B$ 795.4723, found: 795.4703.

Synthesis of 3f: A mixture of **3a** (0.50 g, 0.93 mmol), phenyl acetylene (0.25 mL, 2.3 mmol), $PdCl_2(PPh_3)_2$ (81 mg, 0.10 mmol), CuI (19 mg, 0.10 mmol) and Et_3N (10 mL) was refluxed for 10 h. The mixture was treated with aqueous NH_4Cl and extracted with Et_2O. The extracts were dried over anhydrous Na_2SO_4, and the solvents were removed under reduced pressure. The residue was subjected to column chromatography (SiO_2, eluent: $CHCl_3$-hexane 1:1) and GPLC to give **3f** as yellow solids (0.34 g, 63%). mp 188-190 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.99 (t, *J* = 7.0 Hz, 3H), 1.41-1.56 (m, 4H), 1.66 (quint, *J* = 7.3 Hz, 2H), 2.00 (s, 6H), 2.10 (quint, *J* = 8.0 Hz, 2H), 2.44 (s, 3H), 4.51 (t, *J* = 8.4 Hz, 2H), 7.00 (s, 2H), 7.29-7.39 (m, 6H), 7.57 (dd, *J* = 7.6, 2.0 Hz, 4H), 7.63 (d, *J* = 9.2 Hz, 2H), 7.89 (dd, *J* = 9.2, 2.0 Hz, 2H), 8.04 (d, *J* = 2.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.12, 21.40, 22.78, 23.40, 26.71, 27.38, 31.61, 48.21, 88.76, 89.64, 114.63, 114.97, 123.41, 126.84, 126.93, 127.89, 128.20, 131.43, 136.50, 139.18, 140.89, 144.60; HRMS (FAB$^+$) *m*/*z* calcd for $C_{43}H_{40}N^{11}B$ 581.3254, found 581.3273.

Synthesis of 3g: To a Et_2O (5 mL) solution of **3b** (0.10 g, 0.16 mmol) was added Bu^{t}Li (2.2 M pentane solution) (0.48 mL, 1.0 mmol) at –75 °C, and the solution changed to yellow suspension immediately. The suspension was stirred for 15 min at that temperature. To the suspension was added MeI (0.20 mL, 2.3 mmol), and the mixture was allowed to be warmed to rt and stirred for 1 h. The solution was treated with aqueous NH_4Cl and extracted with benzene. The extracts were dried over anhydrous Na_2SO_4, and the solvents were removed under reduced pressure. The residue was subjected to GPLC to give **3h** as yellow solids (79 mg, 100%). mp 183-185 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.95-0.98 (m, 15H), 1.35-1.51 (m, 10H), 1.62 (quint, *J* = 7.48 Hz, 2H), 2.06 (quint, *J* = 8.0 Hz, 2H), 2.34 (s, 6H), 2.37 (sept, *J* = 6.3 Hz, 2H), 3.01 (sept, *J* = 6.9 Hz, 1H), 4.45 (t, *J* = 8.5 Hz, 2H), 7.07 (s, 2H), 7.49-7.54 (m, 4H), 7.63 (d, *J* = 2.1 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.07, 20.47, 22.73, 24.18, 24.36, 26.73, 27.24, 31.63, 34.12, 34.74, 47.81, 114.05, 119.61, 127.70, 128.20, 134.48, 137.54, 138.35, 143.03, 147.33, 150.43; HRMS (FAB$^+$) *m*/*z* calcd for $C_{35}H_{48}{}^{11}BN$ 493.3880, found: 493.3865.

Synthesis of 2,5-Dibromo-*N*,*N*'-bis(2,4-dibromophenyl)-*N*,*N*'-dihexylbenzene-1,4-diamine (4): A mixture of 2,4-dibromoaniline (11 g, 44 mmol), 1,4-dibromo-2,5-diiobobenzene (10 g, 20 mmol), Bu^{t}ONa (6.4 g, 66 mmol), $Pd(dba)_2$ (1.3 g, 2.3 mmol), DPPF (1.3 g, 2.3 mmol) and toluene (100 mL) was stirred at 100 °C for 3 d. The mixture was treated with aqueous NH_4Cl and extracted with $CHCl_3$. The extracts were dried over anhydrous Na_2SO_4, and the solvents were removed under reduced pressure. The residual black oil was dissolved in THF (500 mL), and to this mixture were added KOH (12 g, 0.21 mol) and $Bu^n{}_4NI$ (1.6 g, 4.3 mmol). The mixture was refluxed for 1 h. To the mixture was added Hex^{n}I (7.8 mL, 53 mmol), and the mixture was refluxed for 2 d. The mixture was treated with aqueous NH_4Cl and extracted with $CHCl_3$. The extracts were dried over anhydrous Na_2SO_4, and the solvents were removed under reduced pressure. The residue was subjected to column chromatography (SiO_2, eluent: $CHCl_3$-hexane 1:10) and recrystallized from $CHCl_3$-EtOH to give **4** as colorless solids (4.7 g, 26%). mp 158-160 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, *J* = 6.6 Hz, 6H), 1.27-1.34 (m, 12H), 1.58 (quint, *J* = 7.4 Hz, 4H), 3.47 (t, *J* = 7.6 Hz, 4H), 6.85 (d, *J* = 8.4 Hz, 2H), 7.08 (s, 2H), 7.35 (dd, *J* = 8.4, 2.0 Hz, 2H), 7.68 (d, *J* = 2.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.08, 22.66, 26.55, 27.67, 31.56, 53.32, 116.51, 119.99, 121.48, 125.60, 130.04, 130.85, 136.69, 143.66, 145,86. Anal. Calcd for $C_{30}H_{34}Br_6N_2$: C, 39.95; H, 3.80; N, 3.11. Found: C, 39.91; H, 3.92; N, 2.99.

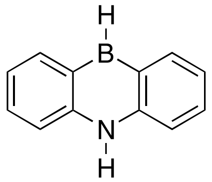
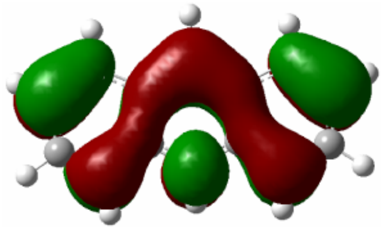
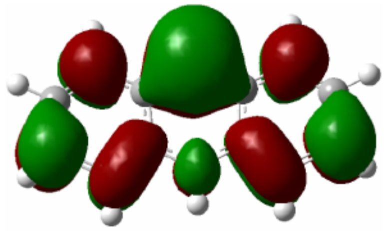
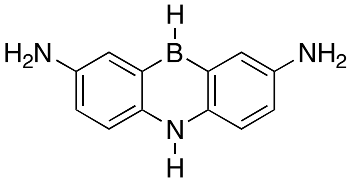
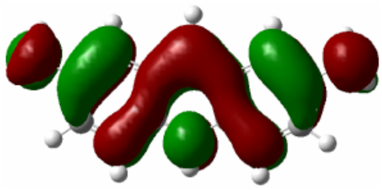
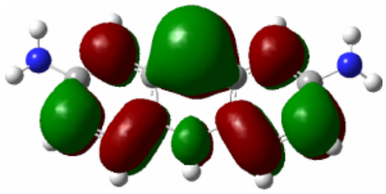
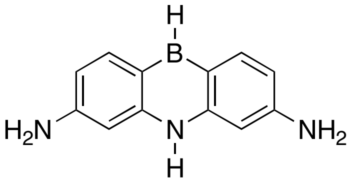
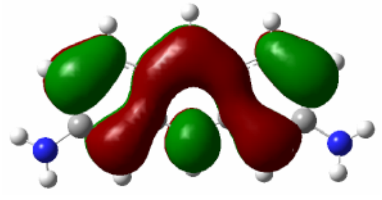
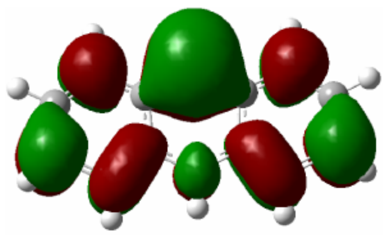
Synthesis of 5b: **4** (0.30 g, 0.33 mmol) was suspended in Et_2O (30 mL), and to this mixture was added Bu^nLi (0.87 mL, 1.4 mmol) at –75 °C. The pale yellow suspension was allowed to be warmed to rt. **4** was gradually dissolved, and the suspension was turned to yellow-colored solution. To this mixture was added $MesB(OMe)_2$ (0.14 mL, 0.66 mmol) at rt, and the mixture was stirred for 10 h. The yellow solution was slowly changed to orange suspension. To the suspension was added aqueous NH_4Cl, and the mixture was stirred for 1 h. The orange precipitates were filtered and transferred to a Schlenck tube, and the orange solids were dried in vacuo. To the Schlenck tube were added Hex^nNH_2 (0.17 mL, 1.3 mmol), Bu^tONa (0.15 g, 1.5 mmol), $Pd(dba)_2$ (8 mg, 13 μmol), BINAP (8 mg, 13 μmol), and toluene (10 mL), and the mixture was stirred at 115 °C for 1 d. The orange suspension became dark red solution immediately after the heating. The mixture was treated with aqueous NH_4Cl and extracted with Et_2O. The extracts were dried over anhydrous Na_2SO_4, and the solvents were removed under reduced pressure. The residue was subjected to GPLC to give **5b** as purple solids (117 mg, 40%). mp 190-193 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 0.89 (t, *J* = 6.7 Hz, 6H), 0.97 (t, *J* = 7.2 Hz, 6H), 1.28-1.38 (m, 24H), 1.58 (quint, *J* = 7.2 Hz, 4H), 1.86 (brs, 4H), 2.04 (s, 12H), 2.44 (s, 6H), 3.09 (brs, 4H), 3.46 (brs, 2H), 4.29 (brs, 4H), 6.98 (s, 4H), 7.14-7.22 (m, 4H), 7.51 (d, *J* = 8.2 Hz, 2H), 7.99 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.05, 14.14, 21.32, 22.62, 22.78, 23.29, 26.59, 26.84, 27.37, 29.66, 31.69, 45.09, 47.79 (One signal corresponding to a methylene carbon atom was not observed due to overlapping.), 115.21, 118.84, 121.30, 122.22, 126.70, 131.44, 135.90, 137.32, 139.29, 139.66, 140.47, 140.73 (One signal corresponding to a ipso-carbon atom to the boron atoms could not be observed due to broadning of the signal.); HRMS (FAB^+) *m*/*z* calcd for $C_{60}H_{84}N_4{}^{11}B_2$ 882.6882, found: 882.6849.

Synthesis of 5c: Intermediate **5a** was prepared from **4** (0.50 g, 0.55 mmol) following the same procedure as **5b**. A mixture of **5a**, $(p\text{-}Bu^t\text{-}C_6H_4)_2NH$ (0.46 g, 1.6 mmol), Bu^tONa (0.16 g, 1.6 mmol), $Pd(dba)_2$ (20 mg, 35 μmol), $PBu^t{}_2$(2-Biph) (15 mg, 50 μmol) and toluene (20 mL) was stirred at 100 °C for 18 h. The mixture was treated with aqueous NH_4Cl and extracted with Et_2O. The extracts were dried over anhydrous Na_2SO_4, and the solvents were removed under reduced pressure. The residue was subjected to GPLC to give **5c** as orange solids (230 mg, 33%). mp 363-365 °C (dec.). ^1H NMR (500 MHz, $CDCl_3$) δ 0.93 (t, *J* = 7.2 Hz, 6H), 1.24-1.36 (m, 48H), 1.86 (br, 4H), 1.96 (s, 12H), 2.31 (s, 6H), 6.75 (s, 4H), 6.96 (d, *J* = 8.7 Hz, 8H), 7.16 (d, *J* = 8.7 Hz, 8H), 7.51 (d, *J* = 9.4 Hz, 2H), 7.54 (dd, *J* = 9.4, 2.4 Hz, 2H), 7.68 (d, *J* = 2.4 Hz, 2H), 8.01 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.10, 21.19, 22.74, 23.37, 26.52, 27.34, 31.42, 31.62, 34.12, 115.48, 121.86, 122.04, 125.68, 126.79, 128.32, 131.90, 133.07, 133.72, 136.00, 136.49, 137.81, 138.65, 139.01, 142.65, 144.21, 145.41. Anal. Calcd for $C_{88}H_{108}B_2N_4$: C, 85.00; H, 8.75; N, 4.51. Found: C, 84.85; H, 8.98; N, 4.43.

Synthesis of 5d: Intermediate **5a** was prepared from **4** (0.30 g, 0.33 mmol) following the same procedure. A mixture of **5a**, 3,6-di-*t*-butyl-9*H*-carbazole (0.28 g, 1.0 mmol), Bu^tONa (0.10 g, 1.0 mmol), $Pd(dba)_2$ (17 mg, 29 μmol), PBu^t_2(2-Biph) (13 mg, 44 μmol) and toluene (10 mL) was stirred at 110 °C for 21 h. The mixture was treated with aqueous NH_4Cl and extracted with Et_2O. The extracts were dried over anhydrous Na_2SO_4, and the solvents were removed under reduced pressure. The residue was subjected to GPLC to give **5d** as orange solids (133 mg, 33%). mp 258-260 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.97 (t, *J* = 6.8 Hz, 6H), 1.31-1.33 (m, 12H), 1.45 (s, 36H), 1.97 (quint, *J* = 7.0 Hz, 4H), 2.01 (s, 12H), 2.34 (s, 6H), 4.43 (t, *J* = 7.0 Hz, 4H), 6.91 (s, 4H), 7.22 (d, *J* = 8.6 Hz, 4H), 7.41 (dd, *J* = 8.6, 1.4 Hz, 4H), 7.78 (d, *J* = 9.6 Hz, 2H), 7.85 (dd, *J* = 9.6, 2.4 Hz, 2H), 8.10 (d, *J* = 2.4 Hz, 2H), 8.11 (d, *J* = 1.4 Hz, 4H), 8.19 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.13, 21.22, 22.79, 23.41, 26.59, 27.43, 31.70, 32.05, 34.71, 48.40, 108.92, 115.94, 116.20, 122.39, 123.00, 123.41, 126.61, 127.06, 128.63, 132.41, 133.24, 135.89, 136.47, 138.20, 138.87, 139.17, 139.92, 142.34, 144.88; LRMS (FAB^+) *m*/*z* 1239 (M^+). Anal. Calcd for $C_{88}H_{106}B_2N_4O$ (M+H_2O): C, 84.06; H, 8.50; N, 4.46. Found: C, 84.13; H, 8.60; N, 4.29.

2. Detail of the theoretical calculations

Theoretical calculations were performed on model compounds shown below. Both optimization and single point energy calculations were carried out at B3LYP/6-31G(d) level of theory.[5] Gaussan03[6] and GaussView03[7] were used for the calculations and molecular orbital plotting, respectively.

	HOMO	LUMO
	 –5.47 eV	 –1.39 eV
	 –4.54 eV	 –1.17 eV
	 –5.19 eV	 –0.74 eV

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