JOURNAL OF Materials CHEMISTRY

Syntheses and emission properties of novel violet-blue emissive aromatic bis(diazaborole)s†

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Received 9th April 2002, Accepted 1st May 2002

Violet-blue emission from novel aromatic bis(diazaborole)s, which were synthesized by the reaction of 2,5-bis(hexyloxy)-1,4-phenylenediboronic acid and 1,2-phenylenediamine derivatives or diaminonaphthalene derivatives, is described. White-blue emission from a 4-methoxy-1,2-phenylenediamine-derived molecule was observed in DMF using 340 nm as the excitation wavelength.

Introduction

Recently, the synthesis and development of π-conjugated oligomers have become important in organic materials science. Poly(aryleneethynylene)s, poly(arylenevinylene)s, and oligoarylenes are useful for new organic materials such as light-emitting diodes, emissive materials, photovoltaic devices, nonlinear optics, two-photon dyes, molecular switches, and molecular wires.[1–4] In the area of emissive materials, blue emissive materials have been reported such as poly(fluorene), poly(*p*-phenylene) (PPP), and so on. Among them, attention has recently been paid to boron containing molecules.[5–10] Boron acts as an acceptor due to its strong electron affinity, so that their band gaps are increased, resulting in blue emission. Moreover, the boron atom makes a bond with carbon and/or a hetero atom using an sp^2 orbital, which results in longer conjugation in the system. However, the main problem is that in general organic boron containing molecules are unstable to air and moisture. In order to obtain stable boron containing molecules, one method is to use bulky groups such as *tert*-butyl and mesityl groups which cause steric hindrance of the boron atom.

Exceptionally, boronic acids are well-known to be stable towards air and moisture. Boronic acids are also well used for molecular recognition of saccharide[11] and as leaving groups for the Suzuki cross-coupling reaction.[12] Herein we will report on the syntheses of novel boron containing molecules derived from boronic acid. Boronic acids are well known to be able to form covalent linkages with diols or 1,2-phenylenediamine.[11] In order to study the usefulness of blue emissive materials derived from boronic acids, we chose 2,5-alkoxy-1,4-phenylenediboronic acid as a key precursor. 2,5-Alkoxy-1,4-phenylenediboronic acids are often used as precursors to, for instance, alkoxy-PPP due to their increased solubility in organic solvents and to insert a twisted angle to shorten the conjugation length of molecules, resulting in a blue emission. 1,2-Phenylenediamine and its derivatives with methoxy and nitrile groups were chosen as other key precursors in order to investigate the effect of donor and/or acceptor groups which might affect the emission properties. We also synthesized other molecules derived from 2,3-diaminonaphthalene and 1,8-diaminonaphthalene. Moreover, these boronic acid-derived molecules would also expected to be stable due to the presence of two boron–nitrogen bonds, which would act like chelate effects. The emission properties of these aromatic bis(diazaborole)s are also described.

Results and discussion

Syntheses of molecules

The desired molecules (**1a**–**1e**) were synthesized according to Schemes 1 and 2. 1,4-Hydroquinone **2** was reacted with 1-hexyl bromide in DMF at 80 °C in the presence of K_2CO_3 to give 1,4-bis(hexyloxy)benzene **3** in 67.2% yield. 1,4-Dibromo-2,5-bis(hexyloxy)benzene **4** was obtained by reaction of **3** and bromine in 92.8% yield. The key precursor, 2,5-bis(hexyloxy)-1,4-phenylenediboronic acid **5**, was synthesized by the lithiation of **4** followed by treatment with trimethoxyborane, then hydrolysis, in 65.8% yield according to a similar procedure in ref. 13. The other key precursors, 1,2-phenylenediamine derivatives, **6** and **7** were commercially available, and **9** was obtained by reduction of **8** in 89.6% yield.[14] Finally, **5** and 1,2-phenylenediamine derivatives were refluxed in toluene (for **1a**) or toluene–triethylamine (for **1b**) or toluene–DMF (for **1c**) to give the desired molecules **1a**–**1c** in 65.8–78.1% yields, respectively. **1d** and **1f** were also synthesized from **5** and 2,3-diaminonaphthalene **10** or 1,8-diaminonaphthalene **11** in 71.3 and 54.0% yield, respectively. In order to study the effect of boron, we also synthesized **1f** as a reference compound by normal Suzuki cross-coupling reaction[12] in 72.7% yield as shown in Scheme 3.

Absorption and emission properties of molecules

The molecules **1a**, **1b**, and **1f** are easily dissolved in dichloromethane, acetone, THF, DMSO, and DMF. On the other hand, **1c**, **1d**, and **1e** hardly dissolved in dichloromethane, and dissolved in DMSO and DMF. Therefore we used DMF for the optical measurements. Absorption and emission spectra of **1a**–**1f** in DMF are shown in Fig. 1 and 2. The optical data are summarized in Table 1. The molecules **1a**–**1c** showed absorption peaks around 350 nm, which was not observed for **1f**,

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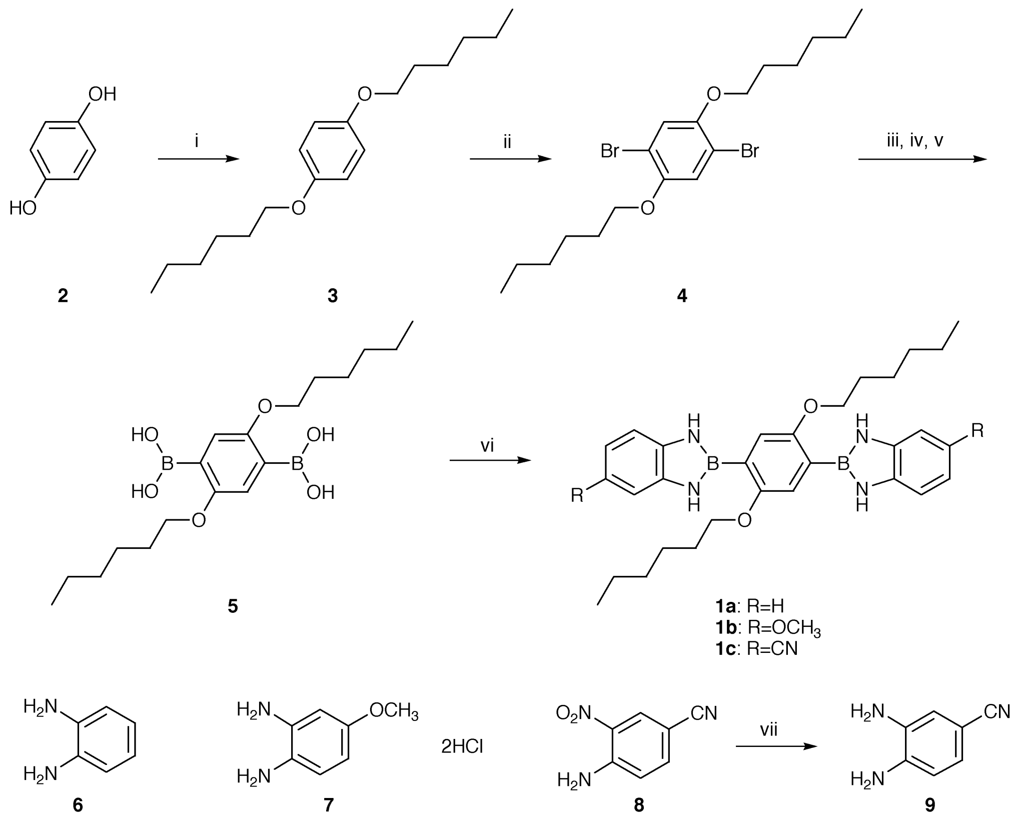
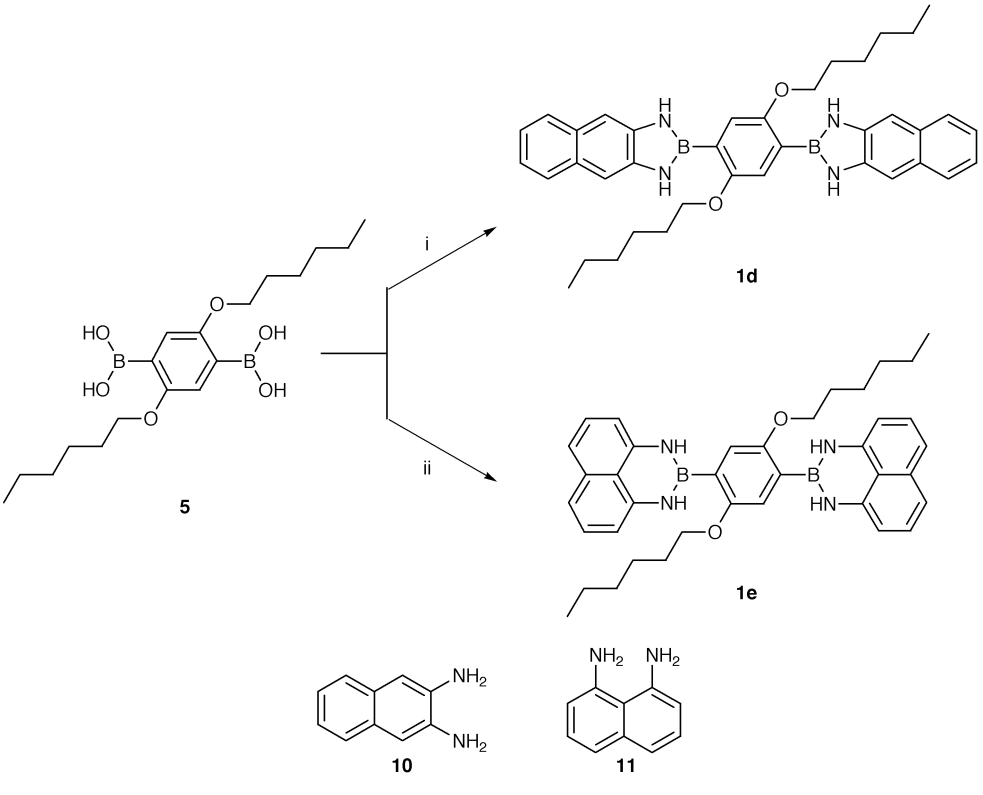
†Electronic supplementary information (ESI) available: pictures of **1a**–**1e** in DMF using 366 nm as excitation wavelength. See http://www.rsc.org/suppdata/jm/b2/b203485a/

DOI: 10.1039/b203485a

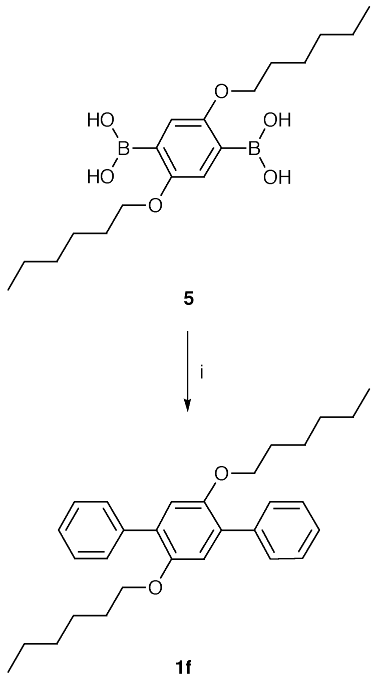


Scheme 1 *Reagents and conditions*: i) hexyl bromide, K_2CO_3, DMF, 80 °C, 67.2%; ii) Br_2, CCl_4, <5 °C, 92.8%; iii) BuLi–hexane, Et_2O, rt; iv) $B(OCH_3)_3$, -40 °C; v) HCl, rt, 70.7%; vi) **6** or **7** or **9**, toluene (for **1a**) or toluene–NEt_3 (for **1b**) or toluene–DMF (for **1c**), reflux, 78.1% (**1a**), 65.8% (**1b**), 75.4% (**1c**); vii) hydrazine monohydrate, ruthenium (5 wt%) on carbon, ethanol, reflux, 89.6%.

indicating that their conjugation lengths are increased compared with that of **1f**. The molecule **1a** showed main two peaks around 315 and 342 nm, respectively. The molecule **1b** showed a main absorption peak around 351 nm, which was red-shifted compared with that of **1a**. This phenomenon would be attributed to the effect of the methoxy group which acts as a donor, resulting in a red-shift of the spectrum. The molecule **1c** showed similar absorption to **1a**. The molecule **1d** showed absorption maxima at 279, 291, 353, and 366 nm. On the other hand, **1e** showed a broad absorption peak around 344 nm. The



Scheme 2 *Reagents and conditions*: i) **10**, toluene, reflux, 71.3%; ii) **11**, toluene, reflux, 54.0%.



Scheme 3 *Reagents and condition*: i) iodobenzene, Pd(PPh$_3$)$_4$, toluene–methanol–2 M Na$_2$CO$_3$ aq., reflux, 72.7%.

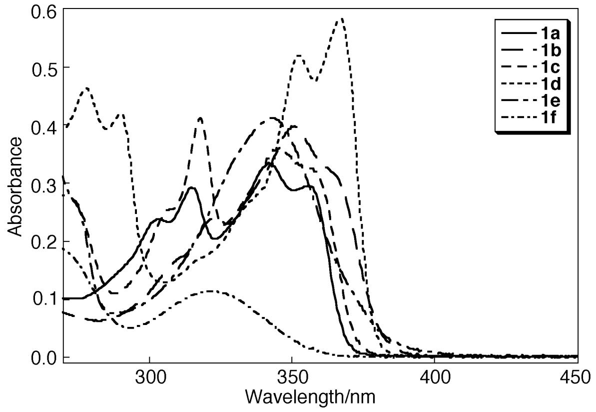


Fig. 1 Absorption spectra of **1a**–**1f** in DMF at rt: [**1a**–**1f**] = 1.0 × 10^{-5} mol dm^{-3}.

emission spectra of **1a**–**1f** were measured using 340 nm as an excitation wavelength. The molecules **1a** and **1c** exhibited violet emission. The emission maxima of **1a** and **1c** were similar to that of **1f** although the emission peaks were split. Interestingly, the emission maxima of **1b** are different from those of **1a** and **1c**, and observed around 438 nm which corresponds to the blue region. The reason why a strong red-shift of **1b**, compared with **1a** and **1c**, was observed is unknown so far; it might be due to increase of the conjugation length, and/or might be produced by charge transfer between the methoxy group and the boron atom. **1d** showed emission peaks at 376, 395, and 417 nm. However, the emission peak of **1e**, a positional isomer of **1d**, could not be observed. From Fig. 2, the emission properties of **1a**–**1e** except for **1b** and **1e**, would be dependent on the boron atom. The relative emission quantum yields of **1a**–**1f** were measured using *p*-terphenyl as a standard (0.92 in cyclohexane at 303 nm as excitation wavelength[15]). The relative emission quantum yield of **1e** could not be determined due to the weak emission intensity. The emission quantum yields of **1a**–**1d** were higher than that of **1f**, indicating that the boron atom will be useful for emissive molecules. The pictures of **1a**–**1e** in DMF using 366 nm as an excitation wavelength (UV-lamp) are shown in the Electronic Supplementary Information† (ESI; **1a**, **1b**, **1c**, **1d**, and **1e** from left to right, respectively). Unfortunately, when we tried to measure the emission spectra of these molecules in the solid state, a spin-coated film could not be prepared due to deposition of the samples on the film.

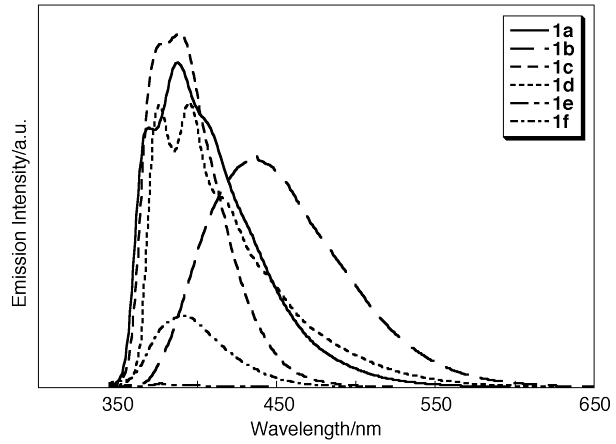


Fig. 2 Emission spectra of **1a**–**1f** in DMF at rt: [**1a**–**1f**] = 1.0 × 10^{-6} mol dm^{-3}; λ_{ex} = 340 nm.

The cyclic voltammograms (CV) of **1a**–**1f** were measured in DMF and the data are summarized in Table 2 (*vs.* Fc/Fc$^+$ in DMF at 298 K[16]). The reduction peaks of **1a**–**1f** were irreversible and too weak probably due to decomposition, so that we could not obtain the reduction potential values. In **1a**–**1c**, the order of the oxidation potential values was **1b** > **1a** > **1c**.

Table 2 The electrochemical data for **1a**–**1f** in DMF at 298K[a]

Compound	E_{red}/V	E_{ox}/V
1a	ND[b]	0.460
1b	ND[b]	0.180
1c	ND[b]	0.756
1d	ND[b]	0.500
1e	ND[b]	0.200
1f	ND[b]	0.740

[a] Fc/Fc$^+$ in DMF at 298K;[16] [b] not observed.

Table 1 The optical data for **1a**–**1f** in DMF at rt

Compound	λ_{abs}/nm[a](log ε/dm^3 mol^{-1} cm^{-1})	λ_{emis}/nm[b,c]	ϕ[e,f]
1a	303 (4.37), 315 (4.46), 342 (4.52), 356 (4.47)	370, 389, 405	0.99 ± 0.01
1b	309 (4.21), 323 (4.38), 351 (4.60), 364 (4.51)	438	0.78 ± 0.03
1c	306 (4.39), 318 (4.61), 347 (4.55), 357 (4.51)	378, 389	0.88 ± 0.01
1d	279 (4.66), 291 (4.62), 353 (4.71), 366 (4.76)	376, 395, 417	0.85 ± 0.04
1e	344 (4.61)	ND[d]	ND[g]
1f	323 (4.05)	392	0.66 ± 0.01

[a] [**1a**–**1f**] = 1.0 × 10^{-5} mol dm^{-3}. [b] [**1a**–**1f**] = 1.0 × 10^{-6} mol dm^{-3}. [c] λ_{ex} = 340 nm. [d] Very weak. [e] Based on *p*-terphenyl in cyclohexane (0.92 at 303 nm as the excitation wavelength). [f] The errors reported are based on the standard deviation values measured in duplicate runs. [g] Not determined.

These phenomena were related to the substituent groups. The oxidation potential of **1f** was larger than those of **1a** and **1d**, indicating that the nitrogen atom would be more easily oxidized compared with the boron atom.

Conclusion

In conclusion, we synthesized organic boron containing violet-blue emissive molecules derived from boronic acid. These molecules would be useful for emissive materials such as EL materials, molecular wires, and so on. Further researches on the application of devices is now under way.

Experimental

Materials

All chemical reagents and dehydrated solvents were commercially available and used without further purification. Analytical thin layer chromatography was performed on commercial Merck plates coated with silica gel $60F_{254}$. Silica gel used for chromatography was Wakogel C300 and Merck silica gel 60. DMF and cyclohexane for fluorimetry were degassed, and nitrogen was bubbled into the solvents for 1 h before use.

Instrumentation

^{1}H NMR spectra were recorded in $CDCl_3$ and/or DMSO-d_6 solutions on a Bruker ARX400 spectrometer (400 MHz). Chemical shifts in $CDCl_3$ are reported in ppm downfield from TMS, and coupling constants are in hertz. FAB-MS spectra were recorded on a JEOL JMS-DX303 mass spectrometer using 3-nitrobenzyl alcohol as a matrix. Elemental analyses were performed at Chemical Analysis Center of AIST. Absorption spectra were recorded on a Jasco V-560. Emission spectra were recorded on a SPEX Fluorolog. The relative emission quantum yields were determined based on *p*-terphenyl in cyclohexane[15] according to the literature procedures.[17] Cyclic voltammetry measurements were performed using BAS100BW under the following conditions: internal standard, ferrocene/ferrocenium; working electrode, Pt disk (25 µm diameter); auxiliary electrode, Pt wire; reference electrode, Ag/$AgNO_3$; solvent, DMF; electrolyte, 0.1 M tetra(*n*-butyl)ammonium hexafluorophosphate; temperature, 298 K.

1,4-Bis(hexyloxy)benzene 3

A mixture of hydroquinone **2** (10.008 g, 63.572 mol) and 1-hexyl bromide (29.0 ml, 0.207 mol) was stirred in DMF (60 ml) in the presence of K_2CO_3 (26.351 g, 0.191 mol) at 80 °C under nitrogen for 1 day. The solution was poured into 300 ml of water, and extracted with chloroform (150 ml) twice. The organic layer was dried with $MgSO_4$, and filtered. The solvent was removed *in vacuo*, and the residue was passed through silica gel using chloroform as eluent. Finally, recrystallization from methanol gave **3** (17.001 g, 67.2%) as crystals.

^{1}H NMR (400 MHz, $CDCl_3$, TMS): (ppm) 0.90 (t, *J* 7.0 Hz, 6H, CH_3), 1.31–1.46 (m, 12H, CH_2), 1.46–1.765 (m, 4H, CH_2), 3.895 (t, *J* 6.6 Hz, 4H, $ArOCH_2$), 6.82 (s, 4H, arom. H).

1,4-Dibromo-2,5-bis(hexyloxy)benzene 4

1,4-Bis(hexyloxy)benzene **3** (17.016 g, 61.113 mol) was dissolved in CCl_4 (75 ml) and stirred below 5 °C. To the solution was added dropwise 8.0 ml (0.155 mol) of bromine over the course of 1 h. The resulting solution was stirred overnight. The remaining bromine was quenched by the addition of Na_2SO_3 aq., then the organic layer was extracted with dichloromethane (50 ml) twice, washed with water (150 ml), dried with $MgSO_4$, and filtered. The solvent was removed *in vacuo*, and the residue was recrystallized from dichloromethane–ethanol to give **4** (24.750 g, 92.8%) as crystals.

^{1}H NMR (400 MHz, $CDCl_3$, TMS): (ppm) 0.91 (t, *J* 7.0 Hz, 6H, CH_3), 1.32–1.52 (m, 12H, CH_2), 1.76–1.83 (m, 4H, CH_2), 3.94 (t, *J* 6.5 Hz, 4H, $ArOCH_2$), 7.08 (s, 2H, arom. H).

2,5-Bis(hexyloxy)-1,4-phenylenediboronic acid 5

1,4-Dibromo-2,5-bis(hexyloxy)benzene **4** (5.008 g, 11.480 mmol) was stirred in Et_2O (30 ml) at rt under nitrogen. To the solution was added a 1.58 M hexane solution of BuLi (20 ml), and the resulting solution was stirred at rt overnight. Trimethoxyborane (5.6 ml, 50.389 mmol) was added to the solution at −40 °C and stirred overnight from −40 °C to rt. The reaction was quenched by the addition of HCl aq., and the resulting precipitate was collected, washed with water, Et_2O, and dried to give **5** (2.971 g, 70.7%) as a white solid.

^{1}H NMR (400 MHz, DMSO-d_6): (ppm) 0.88 (t, *J* 7.0 Hz, 6H, CH_3), 1.29–1.43 (m, 12H, CH_2), 1.69–1.745 (m, 4H, CH_2), 3.99 (t, *J* 6.5 Hz, 4H, $ArOCH_2$), 7.19 (s, 2H, arom. H), 7.80 (s, 4H, OH).

4-Cyano-1,2-phenylenediamine 9

4-Amino-3-nitrobenzonitrile **8** (3.006 g, 18.426 mmol) was reduced in the presence of hydrazine hydrate (4.0 ml, 82.300 mmol) and activated charcoal (0.800 g) in ethanol (60 ml) at reflux until the foam of the reaction mixture became colorless. After being cooled, the reaction mixture was filtered, and the filtrate was evaporated to dryness, giving a white powder.

^{1}H NMR (400 MHz, DMSO-d_6): (ppm) 4.86 (s, 2H, NH_2), 5.44 (s, 2H, NH_2), 6.55 (d, *J* 8.0 Hz, 1H, arom. H), 6.76 (d, *J* 1.8 Hz, 1H, arom. H), 6.80 (dd, *J* 8.0 and 1.9 Hz, 1H, arom. H).

Syntheses of aromatic bis(diazaborole)s

1a. A mixture of 2,5-bis(hexyloxy)-1,4-phenylenediboronic acid **5** (0.703 g, 1.920 mmol) and 1,2-phenylenediamine **6** (0.447 g, 4.015 mmol) was refluxed in toluene (20 ml) under nitrogen for 1 day. After cooling to rt, the resulting precipitate was collected and recrystallized from toluene twice to give product **1a** (0.765 g; 78.1%) as needle-like crystals.

^{1}H NMR (400 MHz, DMSO-d_6): (ppm) 0.89 (t, *J* 7.1 Hz, 6H, CH_3), 1.31–1.525 (m, 12H, CH_2), 1.88–1.95 (m, 4H, CH_2), 4.15 (t, *J* 6.7 Hz, 4H, $ArOCH_2$), 6.82–6.86 (m, 4H, arom. H), 7.11–7.155 (m, 4H, arom. H), 7.51 (s, 2H, arom. H), 8.62 (s, 4H, NH); FAB-MS: m/z = 510 (M^+); Calcd. for $C_{30}H_{40}B_2N_4O_2$: C, 70.61; H, 7.90; N, 10.98; Found. C, 70.31; H, 7.90; N, 10.83%.

1b. 4-Methoxy-1,2-phenylenediamine dihydrochloride **7** (1.560 g, 7.390 mmol) was stirred in toluene (25 ml) in the presence of triethylamine (2.2 ml) at rt under nitrogen for 2 h to hydrolysis. To the solution was added 2,5-bis(hexyloxy)-1,4-phenylenediboronic acid **5** (0.900 g, 2.459 mmol), and the resulting solution was refluxed for 2 days. After cooling to rt, 200 ml of water were added, and the resulting precipitate was collected, washed with water, and dried. Finally, it was recrystallized from toluene–acetone twice to give product **1b** (0.923 g; 65.8%) as fluffy crystals like cotton wool.

^{1}H NMR (400 MHz, DMSO-d_6): (ppm) 0.89 (t, *J* 7.1 Hz, 6H, CH_3), 1.315–1.52 (m, 12H, CH_2), 1.87–1.94 (m, 4H, CH_2), 3.73 (s, 6H, OCH_3), 4.125 (t, *J* 6.7 Hz, 4H, $ArOCH_2$), 6.45 (dd, *J* 8.4 and 2.5 Hz, 2H, arom. H), 6.77 (d, *J* 2.4 Hz, 2H, arom. H), 6.99 (d, *J* 8.4 Hz, 2H, arom. H), 7.465 (s, 2H, arom. H), 8.43 (s, 2H, NH), 8.54 (s, 2H, NH); FAB-MS: m/z = 570 (M^+); Calcd. for $C_{32}H_{44}B_2N_4O_2$: C, 67.39; H, 7.78; N, 9.82; Found. C, 67.44; H, 7.76; N, 9.73%.

1c. A mixture of 2,5-bis(hexyloxy)-1,4-phenylenediboronic acid **5** (0.901 g, 2.461 mmol) and 4-cyano-1,2-phenylenediamine **9** (0.720 g, 5.409 mmol) was refluxed in toluene (30 ml) and DMF (10 ml) under nitrogen for 2 days. After cooling to rt, the resulting precipitate was collected and reprecipitated from DMF–toluene twice to give product **1c** (0.765 g; 78.1%) as a white solid.

^{1}H NMR (400 MHz, DMSO-d_6): (ppm) 0.85 (t, J 6.7 Hz, 6H, CH_3), 1.26–1.49 (m, 12H, CH_2), 1.87–1.935 (m, 4H, CH_2), 4.15 (t, J 6.7 Hz, 4H, ArOCH_2), 7.295–7.32 (m, 4H, arom. H), 7.51 (s, 2H, arom. H), 7.52 (s, 2H, arom. H), 9.05 (s, 2H, NH), 9.31 (s, 2H, NH); FAB-MS: m/z = 560 (M$^+$); Calcd. for $C_{32}H_{38}B_2N_6O_2$: C, 68.60; H, 6.84; N, 15.00; Found. C, 68.20; H, 6.86; N, 14.78%.

1d. A mixture of 2,5-bis(hexyloxy)-1,4-phenylenediboronic acid **5** (0.554 g; 1.513 mmol) and 2,3-diaminonaphthalene **10** (0.500 g; 3.160 mmol) was refluxed in toluene (25 ml) under nitrogen for 2 days. After cooling to rt, the resulting precipitate was collected and reprecipitated from DMF–toluene twice to give product **1d** (0.659 g; 71.3%) as a white solid.

^{1}H NMR (400 MHz, DMSO-d_6): (ppm) 0.89 (t, J 7.1 Hz, 6H, CH_3), 1.32–1.56 (m, 12H, CH_2), 1.92–1.99 (m, 4H, CH_2), 4.20 (t, J 6.8 Hz, 4H, ArOCH_2), 7.23–7.26 (m, 4H, arom. H), 7.52 (s, 4H, arom. H), 7.60 (s, 2H, arom. H), 7.78–7.80 (m, 4H, arom. H), 8.83 (s, 4H, NH); FAB-MS: m/z = 610 (M$^+$); Calcd. for $C_{38}H_{44}B_2N_4O_2$: C, 74.77; H, 7.27; N, 9.18; Found. C, 74.86; H, 7.34; N, 9.13%.

1e. A mixture of 2,5-bis(hexyloxy)-1,4-phenylenediboronic acid **5** (0.801 g, 2.188 mmol) and 1,8-diaminonaphthalene **11** (0.736 g, 4.652 mmol) was refluxed in toluene (30 ml) under nitrogen overnight. After cooling to rt, the resulting precipitate was collected and recrystallized from toluene twice to give product **1e** (0.721 g, 54.0%) as yellow crystals.

^{1}H NMR (400 MHz, DMSO-d_6): (ppm) 0.85 (t, J 7.1 Hz, 6H, CH_3), 1.27–1.395 (m, 8H, CH_2), 1.49–1.56 (m, 4H, CH_2), 1.82–1.87 (m, 4H, CH_2), 4.13 (t, J 6.2 Hz, 4H, ArOCH_2), 6.50 (d, J 7.2 Hz, 4H, arom. H), 6.93 (d, J 8.1 Hz, 4H, arom. H), 7.10 (t, J 7.8 Hz, 4H, arom. H), 7.37 (s, 2H, arom. H), 7.98 (s, 4H, NH); FAB-MS: m/z = 610 (M$^+$); Calcd. for $C_{38}H_{44}B_2N_4O_2$: C, 74.77; H, 7.27; N, 9.18; Found. C, 74.745; H, 7.26; N, 9.15%.

Synthesis of reference molecule.

2,5-Bis(hexyloxy)-1,4-diphenylbenzene 1f. A mixture of 2,5-bis(hexyloxy)-1,4-phenylenediboronic acid **5** (0.901 g, 2.461 mmol), iodobenzene (0.70 ml, 6.308 mmol), and Pd(PPh$_3$)$_4$ (0.145 g, 0.125 mmol) was refluxed in toluene (20 ml)–methanol (10 ml)–2 M Na_2CO_3 aq. (10 ml) under nitrogen for 1 day. After cooling to rt, the organic layer was extracted from toluene (20 ml) three times, washed with water (50 ml), dried with $MgSO_4$ (anhydrous), and filtered. The solvent was evaporated *in vacuo*, and the residue was purified by column chromatography on silica gel using chloroform–hexane (1 : 2 v/v) as eluent. Finally, recrystallization from methanol gave product **1f** (0.770 g; 72.7%) as a white solid.

1f: ^{1}H NMR (400 MHz, $CDCl_3$, TMS): (ppm) 0.86 (t, J 6.9 Hz, 6H, CH_3), 1.20–1.39 (m, 12H, CH_2), 1.64–1.71 (m, 4H, CH_2), 3.90 (t, J 6.5 Hz, 4H, ArOCH_2), 6.985 (s, 2H, arom. H), 7.305–7.345 (m, 2H, arom. H), 7.39–7.43 (m, 4H, arom. H), 7.59–7.615 (m, 4H, arom. H); FAB-MS: m/z = 430 (M$^+$); Calcd. for $C_{30}H_{38}O_2$: C, 83.68; H, 8.89; Found. C, 83.75; H, 8.92%.

Acknowledgement

We thank Professor Dr Xu-tang Tao, Dr Takashi Okubo, and Professor Dr Hiroyuki Sasabe for helpful discussions. One of the authors (S. M.) expresses his gratitude to Japan Science and Technology Corporation (JST) and JSPS for supporting him as a Domestic Research Fellow.

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