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Multicomponent Assembly of Boron-Based Dendritic Nanostructures

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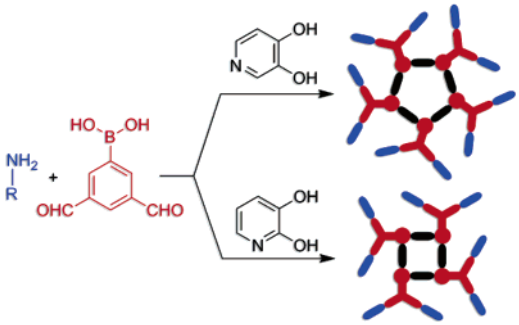

A new synthetic strategy for the construction of boron-based macrocycles and dendrimers is described. Condensation of aryl- and alkylboronic acids with 3,4-dihydroxypyridine is shown to give pentameric macrocycles in which five boronate esters are connected by dative B−N bonds. Three macrocycles have been characterized crystallographically. The boron atoms of these assemblies represent chiral centers, and the assembly process is highly diastereoselective. Attachment of amino or aldehyde groups in the meta position of the arylboronic acid building blocks does not interfere with macrocyclization. This allows performing multicomponent assembly reactions between functionalized boronic acids, dihydroxypyridine ligands, and amines or aldehydes, respectively. Reaction of 3,5-diformylphenylboronic acid, 3,4-dihydroxypyridine, and a primary amine $R-NH_2$ (R = Ph, Bn) gives dendritic nanostructures having a pentameric macrocyclic core and 10 amine-derived R groups in their periphery. Combination of 3,5-diformylphenylboronic acid with 2,3-dihydroxypyridine and the dendron 3,5-(benzyloxy)benzylamine, on the other hand, results in formation of a dendrimer with a tetrameric macrocyclic core and eight dendrons in its periphery.

Introduction

The success of transition-metal-based self-assembly reactions is largely due to the favorable characteristics of metal−ligand interactions: they can be directional and strong yet kinetically labile. As a result it is possible to form highly stable aggregates under thermodynamic control. Beautiful recent examples include a Zn-based Borromean ring,[1] a Ru/Fe-based Sierpinski gasket,[2] Pd-based nanocapsules,[3] and a Ln-based tetrametallic helicate,[4] just to name a few.[5] Similar to transition metals, boron compounds may undergo fast exchange reactions, although the bond energies are typically high. It is thus not surprising that boron compounds are increasingly being investigated in the context of supramolecular chemistry.[6] Considerable effort has been devoted toward the development of boronic-acid-based receptors and sensors.[7] Here, reversible formation of boronates

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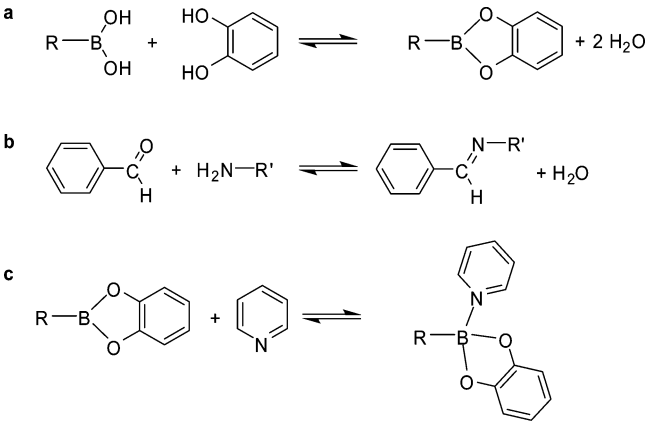
SCHEME 1



is used for molecular recognition of compounds with two or more hydroxyl groups such as carbohydrates. Boron compounds have also been used as a structure-directing element, for example, for the synthesis of discrete macrocycles,[8] helicates,[9] nanotubes,[10] dynamic polymers,[11] and porous covalent organic frameworks.[12] Despite this achievement, it is fair to state that the supramolecular chemistry of boron is largely underdeveloped in comparison with supramolecular coordination chemistry.

In the following we show that condensation reactions involving boronic acids can be used to assemble dendritic nanostructures in a single step. The key point of our strategy is the *parallel utilization of three different reversible reactions*: condensation of boronic acids with aromatic diols (Scheme 1a), condensation of aldehydes with primary amines (Scheme 1b), and addition of N-donor ligands to boronate esters (Scheme 1c). As a result, the process is highly modular. The final structure is obtained by assembly of three chemically distinct compounds, which implies significant structural flexibility.

This type of multicomponent self-assembly, defined here as the assembly of three or more *different* building blocks,[13] is relatively rarely used as a synthetic strategy, at least when formation of a single structurally defined product is the main objective.[14] Several examples have been reported in the field of supramolecular coordination chemistry: metal complexes have been reacted simultaneously with two or more different ligands[15] or vice versa,[16] and imine formation has been employed in parallel to metal−ligand interactions.[17] In the burgeoning field of self-assembled dendrimers,[18] however, multicomponent self-assembly is largely unexplored.[19,20]

Results and Discussion

In a recent communication we reported that boronic acids react with 2,3-dihydroxypyridine ligands to give tetranuclear macrocycles.[8b] These first results prompted us to study reactions

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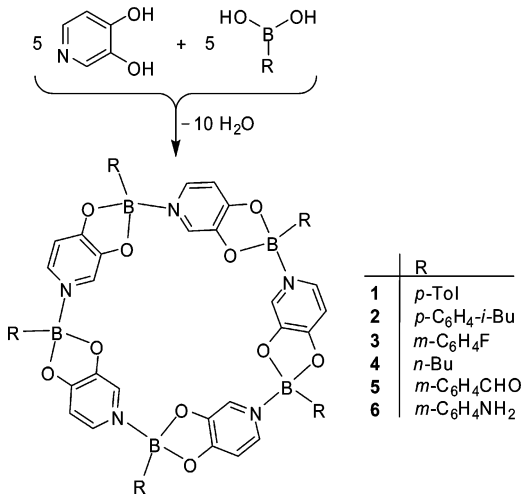
SCHEME 2



	R
1	*p*-Tol
2	*p*-C_6H_4-*i*-Bu
3	*m*-C_6H_4F
4	*n*-Bu
5	*m*-C_6H_4CHO
6	*m*-$C_6H_4NH_2$

with the isomeric ligand 3,4-dihydroxypyridine. When the aryl boronic acids (*p*-Tol)$B(OH)_2$, (*p*-C_6H_4-*i*-Bu)$B(OH)_2$, or (*m*-C_6H_4F)$B(OH)_2$ were reacted with 3,4-dihydroxypyridine in benzene under reflux using a Dean−Stark trap to remove water, the condensation products **1**−**3** were formed in over 80% yield as evidenced by NMR experiments of the crude reaction mixture (Scheme 2). A clean reaction was likewise observed for the aliphatic boronic acid *n*-$BuB(OH)_2$ (**4**). All four products could easily be obtained in pure form by precipitation with pentane.

The NMR spectra of **1**−**4** showed that highly symmetrical structures had formed since only one set of signals was observed for the ligands as well as for the aryl or alkyl side chains of the boronate. In order to obtain further information we investigated **1**, **3**, and **4** by single-crystal X-ray analysis. Pentameric macrocycles were observed for all compounds (Figures 1−3). As expected, the ligand reacted with the boronic acid to give a five-membered cyclic ester. Macrocyclization occurs via dative bonds of the N atoms to the boron atoms of adjacent boronates.[21] With a ring size of 25 atoms, the assemblies are among the largest discrete boron-based macrocycles described so far.[6,8] Furthermore, it should be noted that pentameric macrocycles are rare, not only in the case of boron[22] but also in the case of metal-based macrocycles.[23]

The five boron atoms represent stereogenic centers, all of which have the same configuration. This is in contrast to the tetrameric assemblies formed with 2,3-dihydroxypyridine ligands,

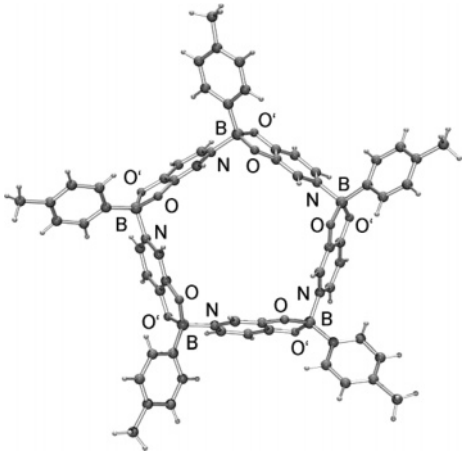


FIGURE 1. Ball-and-stick representation of the molecular structure of **1** in the crystal.

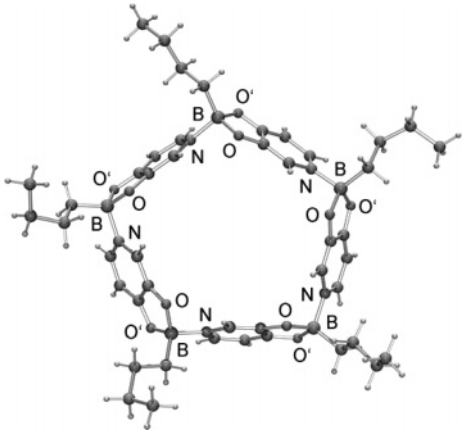


FIGURE 2. Ball-and-stick representation of the molecular structure of **4** in the crystal. The asymmetric unit contains two independent macrocycles, only one of which is shown. The solvent molecules (0.5 C_6H_6 and 0.25 C_5H_{12}) are not shown for clarity.

for which S_4 symmetry with alternating configurations at the boron atoms has been observed.[8b] In the solid state, the two enantiomers of macrocycles **1**, **3**, and **4** form closely packed dimers with intercalating boronate side chains. For compound **1**, this arrangement is depicted in Figure 3.

The average bond distances found for macrocycles **1**, **3**, and **4** are listed in Table 1. With 1.600(16) (**1**), 1.606(12) (**3**), and 1.608(9) Å (**4**), the B−N bonds are shorter than what has been observed for the 4-picoline adducts of phenylcatecholborane (1.651(3) or 1.654(4) Å) or methylcatecholborane (1.660(2) or 1.6444(19) Å).[24] This points to a relatively strong B−N interaction. The B−O bonds of **1** and **3** vary from 1.447(13) to 1.548(9) Å with the bonds to the O′ atom in the 4 position being on average slightly longer than the bonds to the O atom in the

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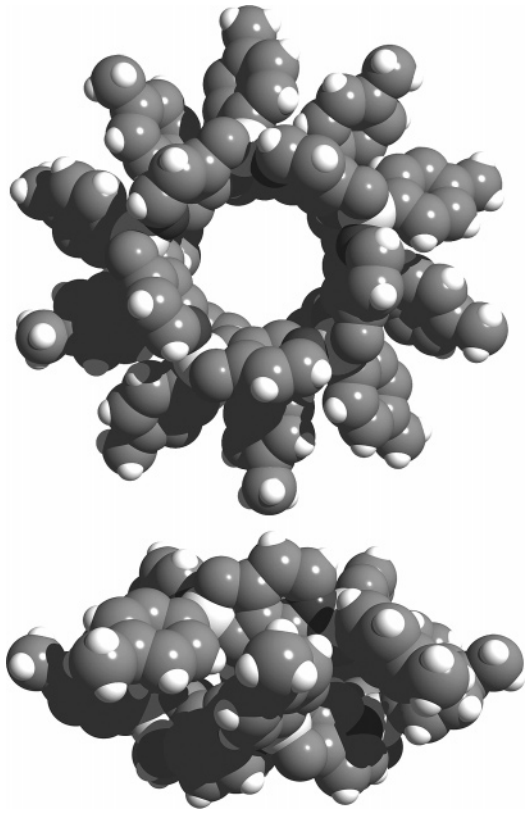
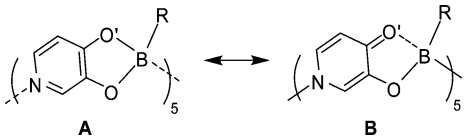


FIGURE 3. Space-filling representation of the two enantiomers of macrocycle **1** in the crystal (view from the side and top). A dimer with intercalating tolyl side chains is observed.

TABLE 1. Selected Average Bond Length for Macrocycles 1, 3, 4 and 7

	B−N	B−O	B−O′	C−O	C−O′
1	1.600(13)	1.509(33)	1.520(17)	1.327(13)	1.331(24)
3	1.606(13)	1.497(7)	1.502(15)	1.346(7)	1.341(13)
4	1.608(11)	1.510(8)	1.523(14)	1.343(14)	1.329(9)
7	1.579(17)	1.513(10)	1.523(10)	1.342(6)	1.314(16)

SCHEME 3



3 position. The carbon−oxygen bond lengths are similar to each other. These values indicate that the mesomeric structure B, in which the bridging ligand is in its pyridonate form, is less important for the overall electronic situation (Scheme 3).

The NMR data of **1**−**4** indicated that the aggregates are stable in solution. The ^{11}B NMR spectra showed broad peaks at around 13 ppm. The upfield shift compared to the typical ^{11}B signals of trigonal planar boronate esters at ∼30 ppm is characteristic for tetracoordinated boron centers.[25] To test the kinetic stability of the assemblies, we mixed equimolar amounts (5 μmol) of the two pentamers **2** and **3** in $CDCl_3$ (0.6 mL). The ^{1}H NMR spectrum of the resulting solution recorded after 15 min was a superposition of the spectra of the pure compounds **2** and **3**.

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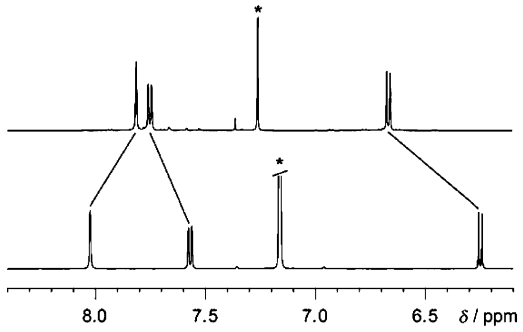


FIGURE 4. Part of the ^{1}H NMR spectrum of the pentamer **4** in $CDCl_3$ (top) or C_6D_6 (bottom). The signals of the solvent molecules are denoted with an asterisk.

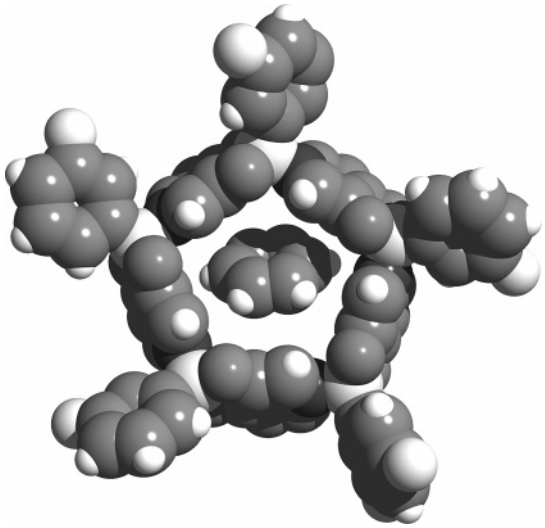


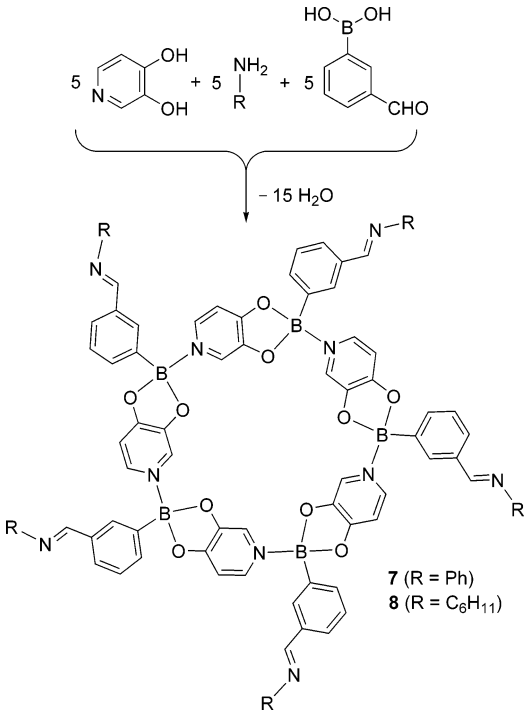
FIGURE 5. Space-filling representation of the molecular structure of **3** and the cocrystallized benzene molecule found in its macrocyclic cavity.

This result cannot be explained by a self-sorting behavior of the macrocycles because a mixture of compounds was obtained when the macrocycles were synthesized using an equimolar amount of (*p*-C_6H_4-*i*-Bu)$B(OH)_2$ and (*m*-C_6H_4F)$B(OH)_2$. It can thus be concluded that exchange reactions of the macrocyclic core are slow on that time scale. This is in agreement with what had been observed for the tetrameric assemblies based on the 2,3-dihydroxypyridine ligands[8b] and may be explained by the strong B−N interaction in these compounds.

NMR spectroscopic investigations of the pentamers **1**−**4** revealed an interesting feature: when the ^{1}H NMR spectra were recorded in C_6D_6 instead of $CDCl_3$, pronounced differences were observed for the chemical shifts of the protons of the bridging pyridine ligands. For compound **4**, the corresponding spectra are depicted in Figure 4. We attribute this difference to ring current effects of a benzene guest molecule in the cavity of the macrocycle. The fact that benzene can be accommodated in the cavity is corroborated by the cocrystallized benzene molecule found inside the macrocycle of crystalline **3** (Figure 5) and in one of the crystallographically distinct macrocycles of crystalline **4**. NMR titration experiments show that these benzene guest molecules are not bound very strongly: addition of 10 equiv

(25) Nöth, H.; Wrackmeyer, B. In *NMR Spectroscopy of Boron Compounds*; Diehl, P., Fluck, E., Kosfeld, R., Eds.; NMR−Basic Principles and Progress 14; Springer-Verlag: Berlin, 1978.

SCHEME 4



of C_6D_6 to a solution of **3** in $CDCl_3$ resulted in only minor changes of the chemical shifts. Marked differences were only observed for significantly higher benzene concentrations.

Having established that condensation of 3,4-dihydroxypyridine and boronic acids gives pentameric assemblies in high yield, we wanted to explore the possibility of using the macrocycles as a scaffold for construction of more complicated structures. Toward this goal, we investigated the reaction of 3,4-dihydroxypyridine with the functionalized boronic acids 3-formylphenylboronic acid and 3-aminophenylboronic acid (Scheme 2). Neither the amino nor the aldehyde group interfered with the assembly process, as evidenced by the NMR spectra of the products **5** and **6**, which were very similar to those of **1**−**4**.

Subsequently, we investigated the three-component condensation of 3-formylphenylboronic acid, 3,4-dihydroxypyridine, and aniline or cyclohexylamine, respectively (Scheme 4). The ^{1}H NMR data of the products **7** and **8** in $CDCl_3$ were in agreement with the structures depicted in Scheme 4. Complete condensation was confirmed by the lack of aldehyde signal at $\delta = 9.99$ ppm and the presence of a singlet for the CH═NR protons at $\delta =$ 8.42 (**7**) and 8.29 (**8**) ppm. The chemical shifts of the pyridine protons of **7** and **8** were similar to what had been observed for assemblies **1**−**6**. Final confirmation of the pentameric structure came from a single-crystal X-ray analysis of compound **7** (Figure 6; Table 1).

The macrocyclic core of **7** is structurally very similar to what was observed for **1**, **3**, and **4**: five boronate esters are bridged via B−N bonds to give a slightly concave macrocycle. The stereogenic boron centers all have the same configurations. In the periphery, we find five benzylidenaniline side chains, all of which have a trans configuration. The diameter (max. H-to-H distance) of the star-shaped compound is 30 Å.

It is possible to reverse the connectivities and condensate 3-aminophenylboronic acid with 3,4-dihydroxypyridine and an aldehyde. This was demonstrated by the synthesis of assembly

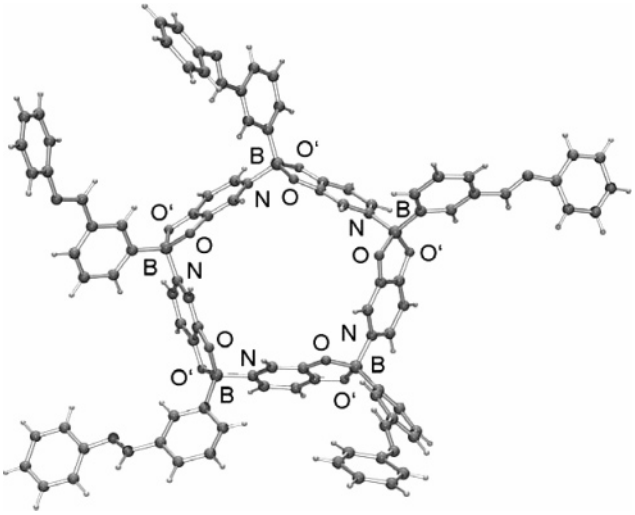
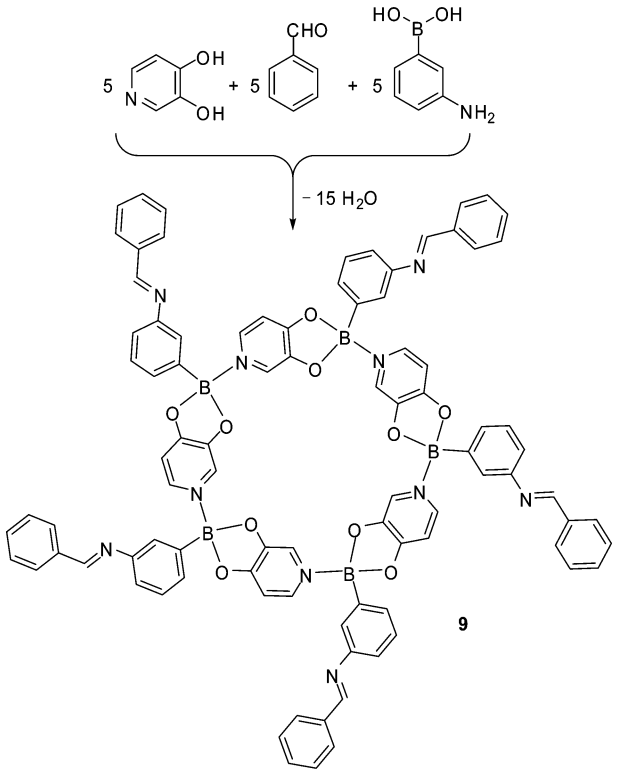


FIGURE 6. Ball-and-stick representation of the molecular structure of **7** in the crystal. The solvent molecules (2 $CHCl_3$ and 0.5 C_5H_{12}) are not shown for clarity.

SCHEME 5

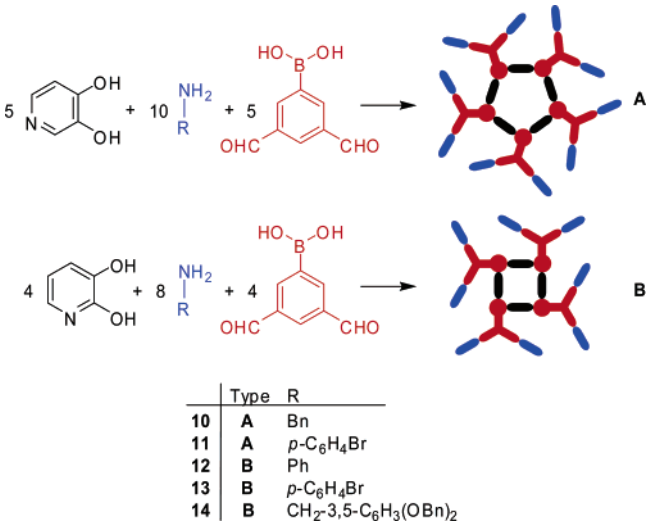


9 (Scheme 5). As compound **7**, it has five benzylidenaniline side chains but the macrocycle is attached to the aniline side.

The possibility to perform aldehyde−amine condensation reactions in parallel to the assembly of the boronate macrocycle suggested that we can use this approach to construct dendritic nanostructures in a single step. Condensation of 3,4-dihydroxypyridine with a primary amine $R-NH_2$ and 3,5-diformylphenylboronic acid should lead to a dendrimer with 10 amine-derived R groups in the periphery and, an analogous reaction with 2,3-dihydroxypyridine should result in a tetrameric structure decorated with 8 amine-derived R groups (Scheme 6).

We tested this approach with several aromatic and aliphatic amines including the small dendron 3,5-(benzyloxy)benzy-

SCHEME 6



	Type	R
10	**A**	Bn
11	**A**	*p*-C_6H_4Br
12	**B**	Ph
13	**B**	*p*-C_6H_4Br
14	**B**	CH_2-3,5-$C_6H_3(OBn)_2$

lamine. In all cases, the expected condensation products **10**−**14** were obtained. Tetramers **12**−**14** were formed almost quantitatively, whereas the crude yield for pentamers **10** and **11** was around 80%. The isolated yields of all products were ∼50%. The purity of the products was determined by elemental analysis and NMR spectroscopy (for an example, see Figure 7). A single signal was observed for the CH═N imine protons, and signals for the aldehyde protons were no longer present. This confirmed complete condensation of the peripheral aldehyde groups with the amines. Evidence for the macrocyclic core structures was the characteristic signals of the bridging oxopyridine ligands. Attempts to characterize the assemblies by mass spectrometry were unfortunately not successful.

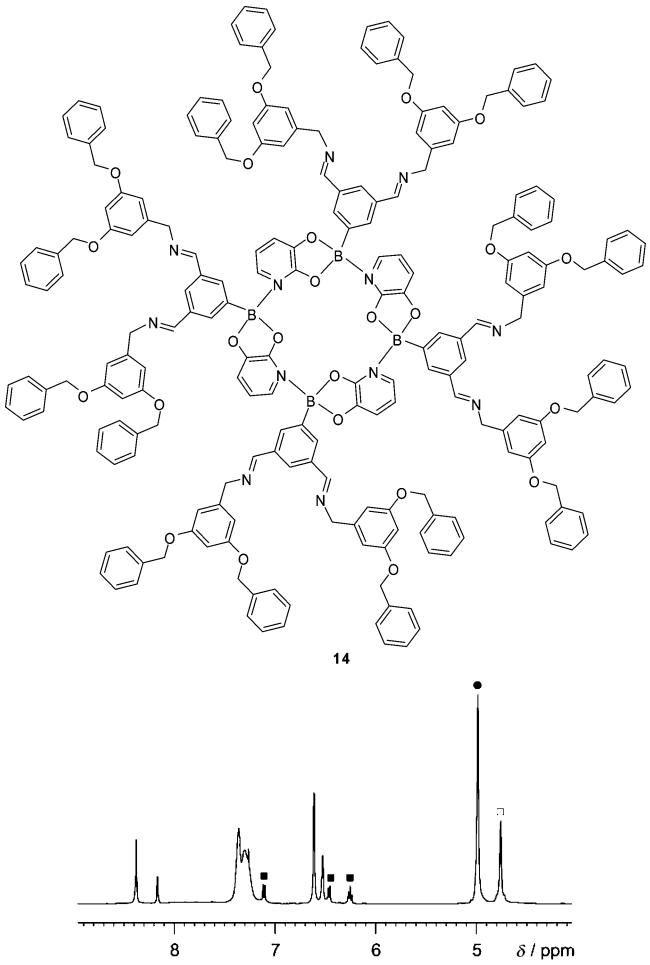


FIGURE 7. ^{1}H NMR spectrum of dendrimer **14** in $CDCl_3$: (■) signals of the bridging pyridine ligands; (□ and ●) signals of the NCH_2 and OCH_2 methylene groups, respectively.

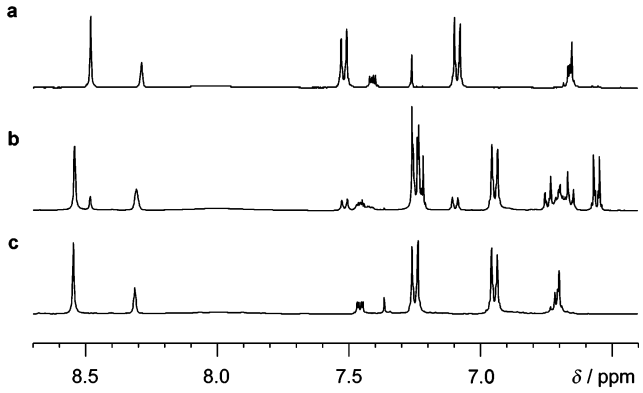


FIGURE 8. Part of the ^{1}H NMR ($CDCl_3$) spectrum of (a) the *p*-bromoaniline-based assembly **13**, (b) a mixture of **13** and 8 equiv of *p*-methoxyaniline after equilibration, and (c) the pure *p*-methoxyaniline-based assembly.

We examined imine exchange reactions in the periphery of the dendritic structures. When 8 equiv of *p*-methoxyaniline was added to a solution of the *p*-bromoaniline-based assembly **13** in $CDCl_3$ (8.3 mM), rapid exchange of the aromatic amines was observed with the equilibrium strongly favoring incorporation of the electron-rich *p*-methoxyaniline (Figure 8). This observation is in line with results from the group of Nitschke, which show that the equilibrium constant of imine exchange reactions involving aniline derivatives can be correlated with the electron-donating abilities of the amine.[26] Attempts to perform similar imine exchange reactions with more basic amines such as benzylamine were not successful. NMR analyses indicated that benzylamine is able to disrupt the pyridine−boron interaction, thereby destroying the macrocyclic core.

Conclusion

In this publication, we describe a new synthetic strategy for construction of boron-based macrocycles and dendrimers. Condensation of aryl- and alkylboronic acids with 3,4-dihydroxypyridine is shown to give pentameric macrocycles in a highly diastereoselective self-assembly process. Macrocycles of this kind can be used as a scaffold for construction of more complicated nanostructures. The basis is the observation that imine condensation reactions can be performed parallel to the macrocyclization reaction. This allows one to carry out multicomponent assembly reactions between functionalized boronic acids, dihydroxypyridine ligands, and amines or aldehydes, respectively. Reaction of 3,5-diformylphenylboronic acid, 3,4-dihydroxypyridine, and a primary amine R−NH_2, for example, gives dendritic nanostructures having a pentameric macrocyclic core and 10 amine-derived R groups in their periphery. Combination of 3,5-diformylphenylboronic acid with 2,3-dihydroxypyridine and dendron 3,5-(benzyloxy)benzylamine, on the other hand, results in formation of a dendrimer with a

(26) Schultz, D.; Nitschke, J. R. *J. Am. Chem. Soc.* **2006**, *128*, 9887−9892.

tetrameric macrocyclic core and eight dendrons in its periphery. The latter represents a rare example of a dendrimer obtained by self-assembly using three chemically distinct building blocks. An intrinsic advantage of our approach is its flexibility. Four, five, eight, or ten different R groups can be attached to a macrocyclic core depending on whether a mono- or bis-functionalized boronic acid is employed and whether 2,3- or 3,4-dihydroxypyridine is used as the bridging ligand. In addition, there seems to be no restriction regarding the directionality of the imine condensation, meaning that the R groups in the periphery can be derived from primary amines or aldehydes. Overall, our results further highlight the potential of boron-based compounds in supramolecular chemistry, a topic likely to receive increasing interest in the future.

Experimental Section

General. 3,4-Dihydroxypyridine was prepared according to literature procedures.[27] 2,3-Dihydroxypyridine and the boronic acids were obtained from commercial sources. All reactions were carried out under an atmosphere of dry nitrogen using standard Schlenck techniques. The ^{1}H, ^{13}C, and ^{11}B spectra were recorded on a 400 MHz spectrometer using the residual protonated solvents (^{1}H, ^{13}C) as internal standards or $BF_3{\cdot}OEt_2$ (^{11}B) as an external standard. All spectra were recorded at room temperature. Only values for hydrogen and nitrogen are reported for the elemental analyses as it is known that incombustible residues may be produced during analysis of boron-containing compounds, which may lead to strong deviations for the carbon value.[7c]

General Procedure for the Synthesis of the Boronate Macrocycles 1−6. A suspension of the respective aryl or alkyl boronic acid (0.5−1.0 mmol) and 3,4-dihydroxypyridine (0.5−1.0 mmol) in freshly distilled benzene (**1**−**5**) or chloroform (**6**) (50−60 mL) was heated under reflux using a Dean−Stark trap. After 4−7 h, the mixture was filtered hot and the filtrate allowed to cool to ambient temperature. Reduction of the volume and/or addition of pentane caused precipitation of a white powder, which was isolated, washed with pentane, and dried under vacuum. **2** precipitated directly from the reaction mixture and was purified analogously to the other complexes. Crystals were obtained by slow diffusion of pentane into a solution of the respective complex in chloroform (**1**) or benzene (**3**, **4**).

[(*p*-Tol)B(C$_5$H$_3$NO$_2$)]$_5$ (1). Yield: 66%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.30 (s, 15H, CH_3), 6.82 (d, ^3J = 6 Hz, 5 H, pyridine), 7.07−7.16 (m, 10 H, phenyl), 7.26 (d, ^3J = 8 Hz, 10 H, phenyl), 7.99 (d, ^3J = 6 Hz, 5 H, pyridine), 8.04 (s, 5 H, pyridine). ^{1}H NMR (400 MHz, C_6D_6): δ 2.19 (s, 15H, CH_3), 6.19 (d, ^3J = 6 Hz, 5 H, pyridine), 7.10−7.26 (m, 10 H, phenyl), 7.58 (d, ^3J = 7 Hz, 10 H, phenyl), 7.71 (d, ^3J = 6 Hz, 5 H, pyridine), 8.11 (s, 5 H, pyridine). ^{13}C NMR (101 MHz, $CDCl_3$): δ 21.5, 106.6, 123.1, 128.7, 131.2, 137.4, 138.0, 152.1, 164.7. ^{11}B NMR (128 MHz, $CDCl_3$): δ 12.7 ($h_{1/2}$ = 700 Hz). Anal. Calcd for $C_{60}H_{50}B_5N_5O_{10}$: H, 4.78; N, 6.64. Found: H, 5.01; N, 6.38.

[(*p*-C$_6$H$_4$-*i*-Bu)B(C$_5$H$_3$NO$_2$)]$_5$ (2). Yield: 86%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.28 (s, 45H, $C(CH_3)_3$), 6.82 (d, ^3J = 6 Hz, 5 H, pyridine), 7.24−7.39 (m, 20 H, phenyl), 8.00 (d, ^3J = 6 Hz, 5 H, pyridine), 8.05 (s, 5 H, pyridine). ^{13}C NMR (101 MHz, $CDCl_3$): δ 31.5, 106.6, 123.2, 124.9, 128.5, 131.0, 137.5, 151.1, 152.1, 164.9. ^{11}B NMR (128 MHz, $CDCl_3$): δ 13.0 ($h_{1/2}$ = 780 Hz). Anal. Calcd for $C_{75}H_{80}B_5N_5O_{10}$: H, 6.33; N, 5.44. Found: H, 6.35; N, 5.46.

[(*m*-C$_6$H$_4$F)B(C$_5$H$_3$NO$_2$)]$_5$ (3). Yield: 31%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.87 (d, ^3J = 6 Hz, 5 H, pyridine), 6.90−6.99 (m, 5 H, phenyl), 7.05−7.16 (m, 10 H, phenyl), 7.20−7.30 (m, 5 H, phenyl), 8.00 (d, ^3J = 6 Hz, 5 H, pyridine), 8.06 (s, 5 H, pyridine). ^{1}H NMR (400 MHz, C_6D_6): δ 6.12 (d, ^3J = 6 Hz, 5 H, pyridine), 6.85−6.93 (m, 5 H, phenyl), 7.04−7.11 (m, 5 H, phenyl), 7.24−7.31 (m, 5 H, phenyl), 7.39−7.48 (m, 5 H, phenyl), 7.57 (d, ^3J = 6 Hz, 5 H, pyridine), 7.98 (s, 5 H, pyridine). ^{13}C NMR (101 MHz, $CDCl_3$): δ 107.0, 115.2 (d, $^2J_{CF}$ = 21 Hz), 117.6 (d, $^2J_{CF}$ = 19 Hz), 123.1, 126.5 (d, $^4J_{CF}$ = 3 Hz), 129.8 (d, $^3J_{CF}$ = 7 Hz), 137.6, 152.0, 163.0 (d, $^1J_{CF}$ = 246 Hz), 164.64. ^{11}B NMR (128 MHz, $CDCl_3$): δ 12.3 ($h_{1/2}$ = 670 Hz). ^{19}F NMR (188 MHz, C_6D_6): δ −113.64. Anal. Calcd for $C_{55}H_{45}B_5F_5N_5O_{10}{\cdot}0.5C_6H_6$: H, 3.44; N, 6.29. Found: H, 3.73; N, 5.88.

[(*n*-Bu)B(C$_5$H$_3$NO$_2$)]$_5$ (4). Yield: 20%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.62−0.71 (m, 10 H, *n*-butyl), 0.79−0.90 (m, 15 H, *n*-butyl), 1.05−1.19 (m, 10 H, *n*-butyl), 1.21−1.34 (m, 10 H, *n*-butyl), 6.67 (d, ^3J = 6 Hz, 5 H, pyridine), 7.75 (d, ^3J = 6 Hz, 5 H, pyridine), 7.81 (s, 5 H, pyridine). ^{1}H NMR (400 MHz, C_6D_6): δ 0.83−1.02 (m, 25 H, *n*-butyl), 1.45−1.61 (m, 20 H, *n*-butyl), 6.25 (d, ^3J = 6 Hz, 5 H, pyridine), 7.57 (d, ^3J = 6 Hz, 5 H, pyridine), 8.02 (s, 5 H, pyridine). ^{13}C NMR (101 MHz, C_6D_6): δ 14.4, 26.3, 27.4, 106.0, 122.8, 136.6, 152.6, 164.9. ^{11}B NMR (128 MHz, C_6D_6): δ 15.5 ($h_{1/2}$ = 770 Hz). Anal. Calcd for $C_{45}H_{60}B_5N_5O_{10}{\cdot}C_5H_{12}$: H, 7.58; N, 7.32. Found: H, 7.84; N, 7.91.

[(*m*-C$_6$H$_4$CHO)B(C$_5$H$_3$NO$_2$)]$_5$ (5). Yield: 51%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.91 (d, ^3J = 6 Hz, 5 H, pyridine), 7.46 (t, ^3J = 8 Hz, 5 H, phenyl), 7.66 (d, ^3J = 7 Hz, 5 H, phenyl), 7.78 (d, ^3J = 8 Hz, 5 H, phenyl), 7.96 (s, 5 H, phenyl), 8.06 (d, ^3J = 6 Hz, 5 H, pyridine), 8.10 (s, 5 H, pyridine), 9.99 (s, 5 H, CHO). ^{13}C NMR (101 MHz, $CDCl_3$): δ 107.2, 123.0, 128.7, 130.0, 132.4, 135.9, 137.3, 137.7, 152.1, 164.7, 193.1. ^{11}B NMR (128 MHz, $CDCl_3$): δ 13.0 ($h_{1/2}$ = 820 Hz). Anal. Calcd for $C_{60}H_{40}B_5N_5O_{15}{\cdot}0.5C_6H_6$: H, 3.72; N, 6.02. Found: H, 3.94; N, 5.59.

[(*m*-C$_6$H$_4$NH$_2$)B(C$_5$H$_3$NO$_2$)]$_5$ (6). Yield: 56%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.57 (b, 10 H, NH_2), 6.61 (d, ^3J = 8 Hz, 5 H, phenyl), 6.71 (s, 5 H, phenyl), 6.76 (d, ^3J = 7 Hz, 5 H, phenyl), 6.82 (d, ^3J = 6 Hz, 5 H, pyridine), 7.09 (t, ^3J = 7 Hz, 5 H, phenyl), 7.98 (d, ^3J = 6 Hz, 5 H, pyridine), 8.04 (s, 5 H, pyridine). ^{13}C NMR (101 MHz, $CDCl_3$): δ 106.6, 115.3, 117.9, 121.4, 123.1, 129.0, 137.5, 146.0, 152.0, 164.6. ^{11}B NMR (128 MHz, $CDCl_3$): δ 13.0 ($h_{1/2}$ = 680 Hz). Anal. Calcd for $C_{55}H_{45}B_5N_{10}O_{10}{\cdot}1.5CHCl_3{\cdot}1.5C_5H_{12}$: H, 4.83; N, 10.40. Found: H, 5.05; N, 9.99.

[(*m*-C$_6$H$_4$CH=NPh)B(C$_5$H$_3$NO$_2$)]$_5$ (7). A suspension of 3-formylphenylboronic acid (150 mg, 1.0 mmol), 3,4-dihydroxypyridine (111 mg, 1.0 mmol), and aniline (112 mg, 1.2 mmol) in distilled benzene (60 mL) was heated under reflux using a Dean−Stark trap. After 6 h, the suspension was filtered hot. The volume of the filtrate was reduced to 10 mL, and pentane (20 mL) was added, which resulted in precipitation of a white solid. The precipitate was filtered, washed with pentane, and dried under vacuum. Yield: 120 mg, 40%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.90 (d, ^3J = 6 Hz, 5 H, pyridine), 7.14−7.22 (m, 15 H, phenyl), 7.31−7.43 (m, 15 H, phenyl), 7.51 (d, ^3J = 7 Hz, 5 H, phenyl), 7.83 (d, ^3J = 8 Hz, 5 H, phenyl), 7.96 (s, 5 H, phenyl), 8.07 (d, ^3J = 6 Hz, 5 H, pyridine), 8.13 (s, 5 H, pyridine), 8.42 (s, 5 H, imine). ^{13}C NMR (101 MHz, $CDCl_3$): δ 107.0, 121.0, 123.2, 125.9, 128.5, 128.8, 129.2, 131.8, 134.3, 135.7, 137.6, 152.1, 152.5, 161.3, 164.7. ^{11}B NMR (128 MHz, $CDCl_3$): δ 13.2 ($h_{1/2}$ = 1060 Hz). Anal. Calcd for $C_{90}H_{65}B_5N_{10}O_{10}$: H, 4.37; N, 9.33. Found: H, 4.67; N, 8.88. Crystals were obtained by slow diffusion of pentane into a solution of **7** in chloroform.

[(*m*-C$_6$H$_4$CH=NCy)B(C$_5$H$_3$NO$_2$)]$_5$ (8). A suspension of 3-formylphenylboronic acid (150 mg, 1.0 mmol), 3,4-dihydroxypyridine (111 mg, 1.0 mmol), and cyclohexylamine (119 mg, 1.2 mmol) in distilled benzene (60 mL) was heated under reflux using a Dean−Stark trap. After 6 h, the suspension was filtered hot. The volume of the filtrate was reduced to one-half, and pentane (30 mL) was added, which resulted in precipitation of a white solid. The precipitate was filtered, washed with pentane, and dried under vacuum. Yield: 77 mg, 25%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.15−1.42 (m, 20 H, cyclohexyl), 1.48−1.88 (m, 30 H, cyclohexyl), 3.10−3.21 (m, 5 H, cyclohexyl), 6.86 (d, ^3J = 6 Hz, 5 H, pyridine), 7.32 (t, ^3J = 8 Hz, 5 H, phenyl), 7.41 (d, ^3J = 7 Hz, 5 H, phenyl),

(27) (a) Ellis, B. L.; Duhme, A. K.; Hider, R. C.; Hossain, M. B.; Rizvi, S.; van der Helm, D. *J. Med. Chem.* **1996**, *39*, 3659−3670. (b) Harris, R. L. N. *Aust. J. Chem.* **1976**, *29*, 1329−1334.

7.64−7.73 (m, 10 H, phenyl), 8.01 (d, ^3J = 6 Hz, 5 H, pyridine), 8.07 (s, 5 H, pyridine), 8.29 (s, 5 H, imine). ^{13}C NMR (101 MHz, $CDCl_3$): δ 25.0, 25.8, 34.5, 70.2, 106.9, 123.1, 127.8, 128.3, 131.3, 133.3, 136.1, 137.6, 152.1, 159.5, 164.7. ^{11}B NMR (128 MHz, $CDCl_3$): δ 13.9 ($h_{1/2}$ = 1000 Hz). Anal. Calcd for $C_{90}H_{95}B_5N_{10}O_{10}$: H, 6.26; N, 9.15. Found: H, 6.52; N, 8.65.

[(*m*-C_6H_4N=CHPh)B($C_5H_3NO_2$)]$_5$ (9). A suspension of 3-aminophenylboronic acid monohydrate (155 mg, 1.0 mmol), 3,4-dihydroxypyridine (111 mg, 1.0 mmol), and benzaldehyde (127 mg, 1.2 mmol) in distilled benzene (60 mL) was heated under reflux using a Dean−Stark trap. After 6 h, the suspension was filtered hot. Upon cooling, a white solid precipitated. The precipitate was filtered, washed with pentane, and dried under vacuum. Yield: 167 mg, 56%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.86 (d, ^3J = 6 Hz, 5 H, pyridine), 7.10 (d, ^3J = 8 Hz, 5 H, phenyl), 7.22−7.28 (m, 5 H, phenyl), 7.32 (t, ^3J = 8 Hz, 5 H, phenyl), 7.39−7.47 (m, 15 H, benzyl), 7.83−7.91 (m, 10 H, benzyl), 8.04 (d, ^3J = 6 Hz, 5 H, pyridine), 8.10 (s, 5 H, pyridine), 8.43 (s, 5H, imine). ^{13}C NMR (101 MHz, $CDCl_3$): δ 106.8, 120.4, 123.2, 123.8, 124.0, 128.5, 128.8, 128.9, 131.3, 136.5, 137.6, 151.7, 152.1, 160.3, 164.7. ^{11}B NMR (128 MHz, $CDCl_3$): δ 11.6 ($h_{1/2}$ = 1170 Hz). Anal. Calcd for $C_{90}H_{65}B_5N_{10}O_{10}\cdot C_6H_6$: H, 4.53; N, 8.87. Found: H, 4.68; N, 8.59.

{**[C_6H_3(CH=NBn)$_2$]B($C_5H_3NO_2$)**}$_5$ **(10).** A suspension of 3,5-diformylphenylboronic acid (89 mg, 0.5 mmol), 3,4-dihydroxypyridine (56 mg, 0.5 mmol), and benzylamine (108 mg, 1.0 mmol) in distilled benzene (80 mL) was stirred at room temperature for 2 h. The suspension was then heated under reflux using a Dean−Stark trap. After 6 h, the solution was allowed to cool. The volume of the filtrate was reduced to 20 mL, and pentane (20 mL) was added, which resulted in precipitation of a white solid. The precipitate was filtered, washed with pentane, and dried under vacuum. Yield: 115 mg, 53%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.80 (s, 20 H, benzyl), 6.85 (d, ^3J = 6 Hz, 5 H, pyridine), 7.21−7.38 (m, 50 H, phenyl), 7.92 (s, 10 H, phenyl), 8.02 (d, ^3J = 6 Hz, 5 H, pyridine), 8.08 (s, 5 H, pyridine or phenyl), 8.10 (s, 5 H, pyridine or phenyl), 8.39 (s, 10 H, imine). ^{13}C NMR (101 MHz, $CDCl_3$): δ 65.2, 107.1, 123.1, 127.1, 128.2, 128.6, 133.3, 133.4, 136.1, 137.6, 139.2, 152.0, 162.3, 164.6. ^{11}B NMR (128 MHz, $CDCl_3$): δ 11.2 ($h_{1/2}$ = 1050 Hz). Anal. Calcd for $C_{90}H_{95}B_5N_{10}O_{10}$: H, 5.14; N, 9.74. Found: H, 5.19; N, 9.35.

{**[C_6H_3(CH=NC_6H_4Br)$_2$]B($C_5H_3NO_2$)**}$_5$ **(11).** A suspension of 3,5-diformylphenylboronic acid (89 mg, 0.5 mmol), 3,34-dihydroxypyridine (56 mg, 0.5 mmol), and 4-bromoaniline (189 mg, 1.1 mmol) in distilled benzene (60 mL) was heated under reflux using a Dean−Stark trap. After 6 h, the suspension was filtered hot. The volume of the filtrate was reduced to 10 mL, and pentane (10 mL) was added, which resulted in precipitation of a white solid. The precipitate was filtered, washed with pentane, and dried under vacuum. Yield: 169 mg, 60%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.45 (d, ^3J = 6 Hz, 5 H, pyridine), 6.68 (d, ^3J = 8 Hz, 20 H, phenyl), 7.36 (d, ^3J = 8 Hz, 20 H, phenyl), 7.60 (s, 5 H, phenyl), 7.72 (s, 10 H, phenyl), 7.82 (s, 5H, pyridine), 8.02 (d, ^3J = 6 Hz, 5 H, pyridine), 9.06 (s, 5 H, imine). ^{13}C NMR (101 MHz, $CDCl_3$): δ 107.4, 119.5, 122.7, 123.6, 129.0, 132.2, 133.8, 135.4, 137.6, 141.8, 150.7, 151.9, 159.8, 164.3. ^{11}B NMR (128 MHz, $CDCl_3$): δ 10.1 ($h_{1/2}$ = 1000 Hz). Anal. Calcd for $C_{125}H_{80}B_5Br_{10}N_{15}O_{10}\cdot 0.5C_6H_6$: H, 2.94; N, 7.39. Found: H, 3.14; N, 6.95.

{**[C_6H_3(CH=NPh)$_2$]B($C_5H_3NO_2$)**}$_4$ **(12).** A suspension of 3,5-diformylphenylboronic acid (178 mg, 1.0 mmol), 2,3-dihydroxypyridine (111 mg, 1.0 mmol), and aniline (224 mg, 2.4 mmol) in distilled benzene (80 mL) was heated under reflux using a Dean−Stark trap. After 6 h, the suspension was filtered hot. The volume of the filtrate was reduced to 10 mL, which resulted in precipitation of a white solid. The precipitate was filtered, washed with pentane, and dried under vacuum. Yield: 224 mg, 56%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.65−6.77 (m, 8 H, pyridine), 7.18−7.29 (m, 24 H, phenyl), 7.34−7.45 (m, 16 H, phenyl), 7.47−7.52 (m, 4 H, pyridine), 8.04 (b, 8 H, phenyl), 8.32 (s, 4 H, phenyl), 8.52 (s, 4 H, imine). ^{13}C NMR (101 MHz, $CDCl_3$): δ 115.7, 118.1, 120.9, 126.2, 127.9, 128.5, 129.5, 130.1, 136.5, 142.0, 150.9, 152.3, 160.4, 163.3. ^{11}B NMR (128 MHz, $CDCl_3$): δ 13.6 ($h_{1/2}$ = 960 Hz). Anal. Calcd for $C_{100}H_{72}B_4N_{12}O_8$: H, 4.50; N, 10.42. Found: H, 4.54; N, 10.07.

{**[C_6H_3(CH=NC_6H_4Br)$_2$]B($C_5H_3NO_2$)**}$_4$ **(13).** A suspension of 3,5-diformylphenylboronic acid (71 mg, 0.40 mmol), 2,3-dihydroxypyridine (44 mg, 0.40 mmol), and 4-bromoaniline (165 mg, 0.96 mmol) in distilled benzene (60 mL) was heated under reflux using a Dean−Stark trap. After 6 h, the suspension was filtered hot. The volume of the filtrate was reduced to 20 mL, and pentane (15 mL) was added, which resulted in precipitation of a white solid. The precipitate was filtered, washed with pentane, and dried under vacuum. Yield: 158 mg, 71%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.60−6.72 (m, 8 H, pyridine), 7.09 (d, ^3J = 9 Hz, 16 H, phenyl), 7.31−7.43 (m, 4 H, pyridine), 7.52 (d, ^3J = 8 Hz, 16 H, phenyl), 8.03 (b, 8 H, phenyl), 8.28 (s, 4 H, phenyl), 8.48 (s, 4 H, imine). ^{13}C NMR (101 MHz, $CDCl_3$): δ 115.6, 116.9, 118.0, 119.7, 122.5, 127.9, 130.4, 132.2, 132.6, 136.3, 142.0, 150.9, 160.6, 163.3. ^{11}B NMR (128 MHz, $CDCl_3$): δ 12.3 ($h_{1/2}$ = 850 Hz). Anal. Calcd for $C_{100}H_{64}B_4Br_8N_{12}O_8$: H, 2.87; N, 7.49. Found: H, 2.98; N, 7.47.

{**[C_6H_3(CH=NC$H_2C_6H_3$(OBn)$_2$)$_2$]B($C_5H_3NO_2$)**}$_4$ **(14).** A suspension of 3,5-diformylphenylboronic acid (36 mg, 0.2 mmol), 2,3-dihydroxypyridine (22 mg, 0.2 mmol), and 3,5-bis(benzyloxy)-benzylamine (128 mg, 0.4 mmol) in distilled benzene (80 mL) was stirred at room temperature for 2 h. The suspension was then heated under reflux using a Dean−Stark trap. After 6 h, the solution was allowed to cool. The volume of the filtrate was reduced to 10 mL, and pentane (15 mL) was added, which resulted in precipitation of a slightly brown solid. The precipitate was filtered, washed with pentane, and dried under vacuum. Yield: 86 mg, 46%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.76 (s, 16 H, benzyl), 4.99 (s, 32 H, benzyl), 6.25 (t, ^3J = 7 Hz, 4 H, pyridine), 6.46 (d, ^3J = 7 Hz, 4 H, pyridine), 6.52 (s, 8 H, phenyl), 6.61 (s, 16 H, phenyl), 7.11 (d, ^3J = 7 Hz, 4 H, pyridine), 7.16−7.47 (m, 40 H, phenyl), 7.96 (b, 8 H, phenyl), 8.16 (s, 4 H, phenyl), 8.37 (s, 8 H, imine). ^{13}C NMR (101 MHz, $CDCl_3$): δ 65.4, 70.1, 100.8, 107.6, 115.4, 118.0, 127.7, 128.1, 128.6, 136.1, 136.9, 141.5, 150.5, 160.2, 162.2, 163.0. ^{11}B NMR (128 MHz, C_6D_6): δ 10.4 ($h_{1/2}$ = 1320 Hz). Anal. Calcd for $C_{220}H_{184}B_4N_{12}O_{24}$: H, 5.42; N, 4.91. Found: H, 5.18; N, 4.86.

Crystallographic Investigations. The relevant details of the crystals, data collection, and structure refinement can be found in the Supporting Information (cif file). Diffraction data were collected using Mo Kα radiation on different equipment and at different temperatures: a 4-circle kappa goniometer equipped with an Oxford Diffraction KM4 Sapphire CCD (**1**, **3**) or a Bruker APEX II CCD (**4**, **7**). Data were reduced by CrysAlis RED 1.7.1[28] (**1**, **3**) and EvalCCD (**4**, **7**).[29] Absorption correction was applied to the data sets of **3** and **7** using a semiempirical method.[30] All structures were refined using full-matrix least-squares on F^2 with all non-H atoms anisotropically defined. The hydrogen atoms were placed in calculated positions using the "riding model" with $U_{iso} = aU_{eq}$ (where a is 1.5 for methyl hydrogen atoms and 1.2 for others). Structure refinement and geometrical calculations were carried out on all structures with SHELXTL.[31] Some serious problems dealing with possible solvent molecules have been encountered during refinement of compound **1**. The data were squeezed[32] and refinement completed. Disorder problems have been found for compound **3**, **4**, and **7** and treated by applying some restraints and constraints. An additional twinning problem appeared in refinement of com-

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pound **4**, which was solved using the twin law for monoclinic simulating orthorhombic (TWIN 1 0 0 0 −1 0 0 0 −1, BASF = 0.262(2)).

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Supporting Information Available: Crystallographic data in CIF format for compounds **1**, **3**, **4**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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