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Self-Assembly of Arylboronate Esters with Pyridyl Side Chains

Erin Sheepwash,[a] Kai Zhou,[a] Rosario Scopelliti,[a] and Kay Severin*[a]

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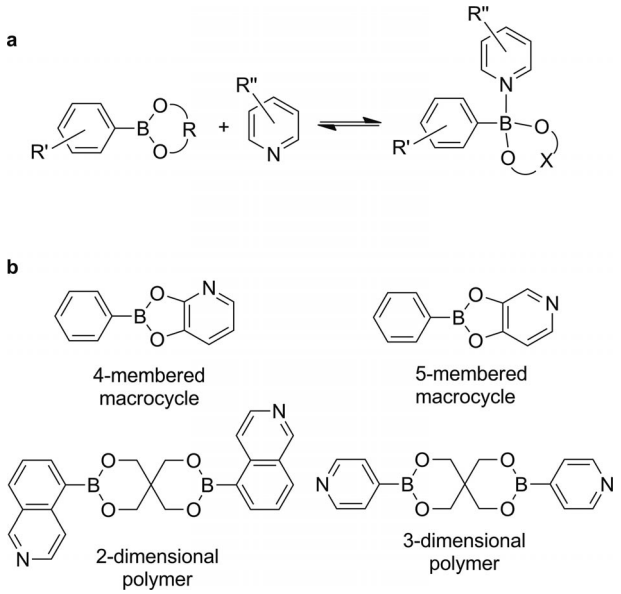
Boronate esters that contain N-donor groups are self-complementary structures, which can assemble by means of dative boron–nitrogen bonds to form macrocycles or polymers. Herein, we describe the synthesis of dioxaborinanes and benzodioxaboroles containing pyridyl side chains. In the solid state, the dioxaborinanes were found to exist predominantly as monomers. Upon crystallization, aggregation into one-dimensional polymers was observed, but only for boronate esters that contained electron-withdrawing groups. The more Lewis acidic benzodioxaboroles, on the other hand, were found to form macrocycles both in solution and in the solid state.

Introduction

N-Donor ligands such as pyridines can bind to Lewis acidic boronate esters by means of dative boron–nitrogen bonds (Scheme 1, a).[1] The stability of the resulting adducts depends on steric and electronic factors, as well as on the nature of the solvent.[2] For the coordination of pyridine to 2-phenylbenzo-1,3,2-dioxaborole (the condensation product of phenylboronic acid and catechol), an association constant of K_a = 51 M^{-1} was determined in benzene.[2a] Significantly higher values ($K_a \geq 10^6$ M^{-1}) are obtained if electron-deficient boronate esters are combined with highly Lewis basic N-donors [e.g., 4-(dimethylamino)pyridine].[2] Dative B–N bonds between boronate esters and N-donor ligands can be used for the construction of molecularly defined nanostructures and polymeric materials.[3] Two different synthetic strategies have been employed in this context: (a) the combination of polytopic boronate esters and (poly)pyridyl ligands,[4–8] and (b) the self-assembly of boronate esters that contain N-donor groups.[9–11] The latter strategy is less explored and only few examples have been described so far. Boronate esters obtained by condensation of phenylboronic acid and dihydroxypyridines were found to form four- and five-membered macrocycles (Scheme 1, b).[9,10] The condensation products of 5-isoquinolinyl- or 4-pyridylboronic acid and pentaerythritol, on the other hand, gave two- and three-dimensional network structures.[11] These crystalline polymers are structurally related to covalent organic frameworks, a class of compounds that has received considerable interest in recent years.[12] Below we describe the synthesis and self-assembly of novel dioxaborinanes and benzodioxaboroles containing pyridyl side chains. These compounds can self-assemble to form macrocycles or one-dimensional polymers.



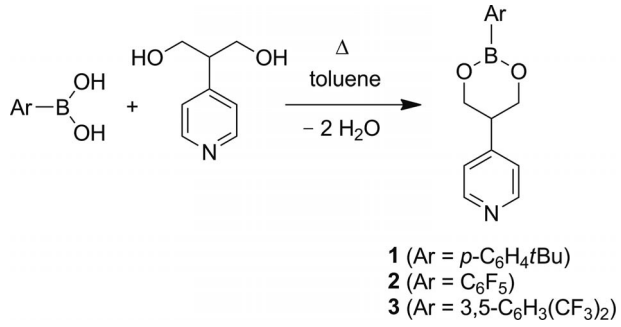
Scheme 1. (a) Pyridyl ligands coordinate to Lewis acidic arylboronate esters through dative B–N bonds; (b) the self-assembly of boronate esters containing N-donor groups gives macrocycles or polymers.

Results and Discussion

The synthesis of dioxaborinanes containing pyridyl side chains was achieved by condensation of 2-(4-pyridyl)prop-

[a] Institut des Sciences et Ingénierie Chimiques, École Polytechnique Fédérale de Lausanne (EPFL), 1015 Lausanne, Switzerland
Fax: +41-21-693-9305
E-mail: kay.severin@epfl.ch
Homepage: lcs.epfl.ch

ane-1,3-diol with different arylboronic acids in toluene under reflux by using a Dean–Stark trap to remove the by-product water (Scheme 2). The products **1**–**3** were obtained in the form of white powders in 50–73% yield by precipitation with pentane. The three esters were characterized by NMR spectroscopy, elemental analyses, and single-crystal X-ray analyses. For the solution-based analyses, the ^{11}B NMR spectroscopic data are of special interest because the chemical shift of the ^{11}B NMR spectroscopic signal gives a strong indication of whether or not the boronate ester is trigonal planar or tetrahedral.[13] In $CDCl_3$, the dioxaborinanes show broad signals at δ = 27.9 (**1**), 18.5 (**2**), and 26.7 ppm (**3**). These values suggest that **1** and **3** exist predominantly as monomers in solution. The value observed for **2** is in between the typical values for trigonal planar and tetrahedral boronate esters.[13] Apparently, partial aggregation occurs in solution, with fast exchange between trigonal and tetrahedral boronate esters.



Scheme 2. Synthesis of the dioxaborinanes **1**, **2**, and **3**.

In the solid state, dioxaborinane **1** exists as a monomer, whereas aggregation through dative B–N bonds is observed for **2** and **3** (Figure 1). The high propensity of **2** and **3** to form B–N adducts is not surprising, given that the fluoro substituents on the aryl groups enhance the Lewis acidity of the boron centers. Aggregates **2** and **3** both show a one-dimensional polymeric structure.[14] The pentafluorophenyl groups of **2** are oriented towards the same side of the polymer strand, whereas adjacent 3,5-(trifluoromethyl)phenyl groups in **3** are rotated about 90° with respect to each other. The observed B–N [**2**: 1.690(3) Å; **3**: 1.666(10) Å] and B–O bond lengths (1.438–1.464 Å) are within the expected range. There are noteworthy structural differences between monomeric **1** and polymeric **2** and **3**. As a result of the trigonal planar boron center, the dioxaborinane ring in **1** adopts an envelope conformation, with five of the six atoms occupying approximately the same plane. The dioxaborinanes in **2** and **3**, on the other hand, adopt a chair conformation. As expected, the B–O bond lengths in **1** [1.3712(12) Å] are shorter than those found for **2** and **3**.

From the results summarized above, it can be concluded that dioxaborinanes are not sufficiently Lewis acidic for significant self-aggregation in solution. In the solid state, polymers could be obtained, but only if boronate esters with electron-withdrawing side chains were employed.

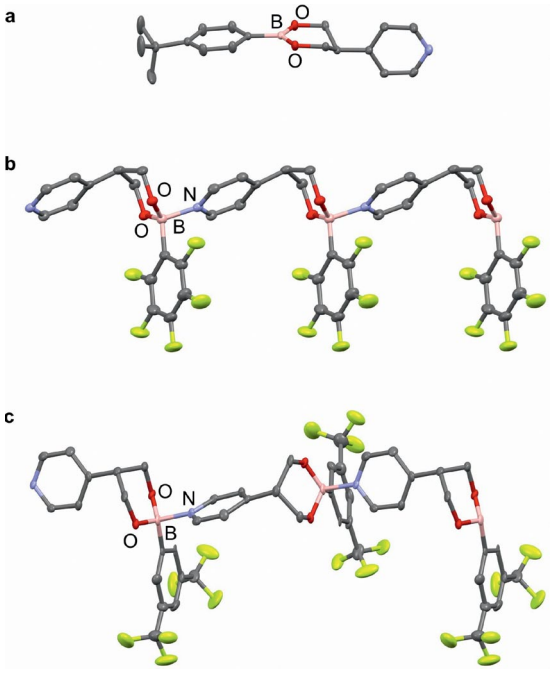
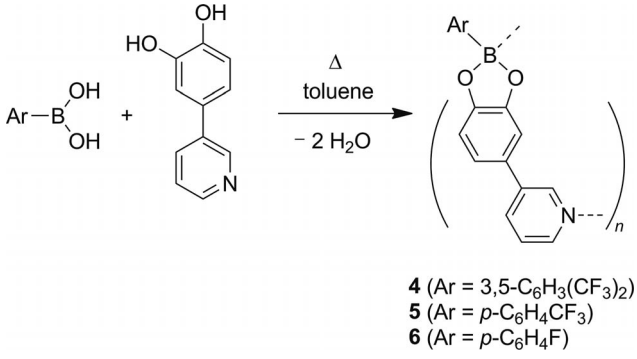


Figure 1. Molecular structures of (a) **1**, (b) **2**, (c) and **3** in the solid state. For polymeric **2** and **3**, only three repeating units are shown. Hydrogen atoms and solvent molecules are omitted for clarity.

To obtain aggregates with enhanced stability, we decided to use more Lewis acidic benzodioxaboroles instead of dioxaborinanes. Thus, the boronate esters **4**–**6** were prepared in 35–46% yield by condensation of different boronic acids with 4-(3-pyridyl)catechol in toluene under reflux conditions (Scheme 3). Boronic acids with electron-withdrawing fluoro substituents were used in all cases.



Scheme 3. Synthesis of the benzodioxaboroles **4**, **5**, and **6**.

The first evidence of the formation of stable aggregates was obtained by ^{11}B NMR spectroscopy: the spectra of **4**, **5**, and **6** in $CDCl_3$ showed broad peaks at δ = 10.7, 14.7, and 15.6 ppm, respectively, thus indicating the predominance of tetracoordinated boron. A crystallographic analysis of **4** revealed the formation of a trimeric macrocycle in the solid state (Figure 2). The macrocycle displays a concave geometry with the three 3,5-trifluoromethylbenzene groups positioned on the same side. The three boron centers possess the same chirality (either *RRR* or *SSS*). In the crys-

tal, these two enantiomers form a dimer, in which the aryl side chains are interdigitated (Figure 2). The dative B–N bonds, which connect the three monomers, exhibit an average bond length of 1.63 Å. This distance is noticeably shorter than what was observed for polymer **2** and **3**.

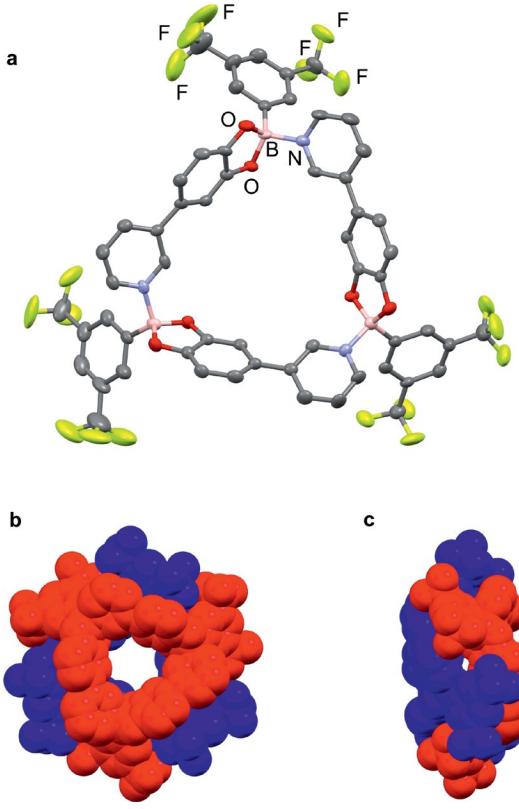
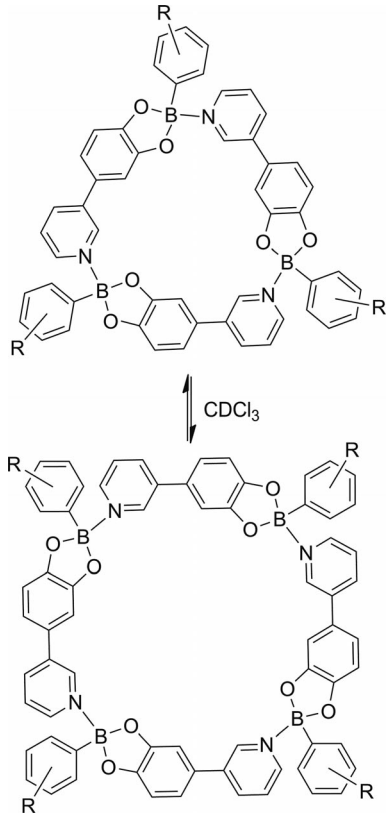


Figure 2. Molecular structures of **4** in the solid state. (a) ORTEP representation; (b) and (c) space-filling representations of the interdigitated enantiomeric macrocycles. Hydrogen atoms (a) and solvent molecules are omitted for clarity.

A closer inspection of the NMR spectroscopic data revealed that the situation in solution is more complex. The ^{1}H NMR spectrum of **4** in $CDCl_3$ or C_6D_6 shows the presence of two different species, the ratio of which is dependent on the concentration. The ^{11}B NMR spectroscopic signal at δ = 10.7 ppm ($CDCl_3$) is in line with tetrahedral boron and excludes the possibility of monomeric **4** (the two species detected by ^{1}H NMR spectroscopy are not resolved in the ^{11}B NMR spectrum). The formation of a dimer is unlikely due to the steric constraints. The concentration dependence of the spectra could be modeled by assuming a dynamic equilibrium between a trimer and tetramer (Scheme 4). An equilibrium constant of K_e(**4**) = [tetramer]^3/[trimer]^4 = 1.8×10^2 M^{-1} was obtained by integration of selected ^{1}H NMR spectroscopic signals at 298 K. Increasing the temperature accelerated the exchange rate between trimer and tetramer. At 323 K, only one set of signals was observed, with a coalescence temperature of around 313 K. Similar results were obtained for **5** (representative spectra are shown in Figure 3) and **6**. However, coalescence was observed at lower temperatures (**5** at ca. 293 K; **6** at ca. 273 K) and measurements at reduced temperature were needed to determine the constants for the tetramer–trimer equilibrium. The following values were obtained: K_e(**5**) = 3.1×10^3 M^{-1} and K_e(**6**) = 2.5×10^3 M^{-1} (both determined at 263 K). Attempts to characterize **5** and **6** by single-crystal X-ray analysis or mass spectrometry were unfortunately not successful.



Scheme 4. In $CDCl_3$, the benzodioxaboroles **4**, **5**, and **6** form a dynamic mixture of trimeric and tetrameric macrocycles.

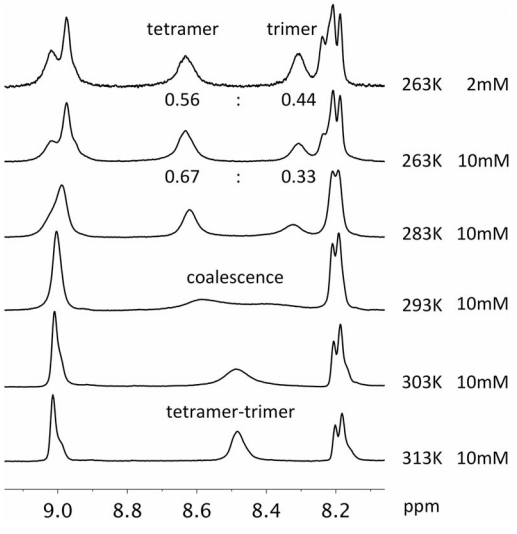


Figure 3. Parts of the ^{1}H NMR spectra of compound **5** in $CDCl_3$ at different temperatures and concentrations.

Conclusion

Dative boron–nitrogen bonds are increasingly being used in the context of structural supramolecular chemistry and crystal engineering. One synthetic strategy involves the utilization of self-complementary building blocks that contain Lewis acidic boron centers along with Lewis basic N-donor ligands. We have explored the self-assembly of novel dioxaborinanes and benzodioxaboroles that contain pyridyl side chains. The modest Lewis acidity of the dioxaborinanes was found to prevent significant aggregation in solution. In the solid state, however, one-dimensional polymers were obtained upon utilization of electron-withdrawing side chains. The benzodioxaboroles, on the other hand, formed dynamic mixtures of trimeric and tetrameric macrocycles in solution. For one compound, we were able to confirm a macrocyclic structure in the solid state by X-ray crystallography. Overall, our results highlight the importance of electronic effects for the assembly of supramolecular structures by means of dative B–N bonds.

Experimental Section

General: The solvents were dried with a solvent purification system from Innovative Technologies, Inc. All reactions were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques. ^{1}H, ^{13}C, ^{11}B, and ^{19}F NMR spectra were obtained with a Bruker Avance instrument (^{1}H: 400 MHz, ^{13}C: 100.6 MHz, ^{11}B: 128.4 MHz, ^{19}F: 188.3 MHz) in $CDCl_3$. ^{1}H chemical shifts (δ) are reported in parts per million referenced to internal $CHCl_3$ (δ = 7.26 ppm). ^{13}C chemical shifts are reported in ppm and referenced to internal $CHCl_3$ (δ = 77.0 ppm). All the NMR spectra were measured at 298 K unless mentioned otherwise. Combustion analyses were performed with a Thermo Scientific Flash 2000 Organic Elemental Analyzer.

Compound 1: A mixture of 2-(4-pyridyl)propan-1,3-diol (34.5 mg, 225 μmol) and (4-*tert*-butylphenyl)boronic acid (40.1 mg, 225 μmol) in toluene (45 mL) was heated under reflux conditions with a Dean Stark apparatus for 3 h. After this time, the mixture was allowed to cool to room temperature, the solvent was reduced to <5 mL, and pentane (10 mL) was added to induce precipitation of the product. The product was filtered, washed with pentane, and residual solvent was removed under vacuum to give **1** as a white solid (33 mg, 50%). Crystallization was accomplished by slow diffusion of pentane into a concentrated solution of **1** in benzene. ^{1}H NMR ($CDCl_3$): δ = 8.59 (dd, J = 4.5, 1.8 Hz, 2 H), 7.74 (d, J = 8.2 Hz, 2 H), 7.40 (d, J = 8.2 Hz, 2 H), 7.19 (dd, J = 4.5, 1.8 Hz, 2 H), 4.34 (dd, J = 11.1, 4.5 Hz, 2 H), 4.23 (t, J = 10.6 Hz, 2 H), 3.30 (m, 1 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 154.1, 150.3, 146.7, 133.7, 124.6, 123.0, 65.8, 42.3, 34.8, 31.2 (B–C was not observed) ppm. ^{11}B NMR ($CDCl_3$): δ = 27.9 ppm. $C_{18}H_{22}BNO_2$ (295.19): calcd. C 73.24, H 7.51, N 4.75; found C 73.25, H 7.43, N 4.86.

Compound 2: A mixture of 2-(4-pyridyl)propan-1,3-diol (34.5 mg, 225 μmol) and (2,3,4,5,6-pentafluorophenyl)boronic acid (47.7 mg, 225 μmol) in toluene (45 mL) was heated under reflux conditions with a Dean Stark apparatus for 3 h. After this time, the mixture was allowed to cool to room temperature. Compound **2** precipitated in the form of an off-white solid. The product was filtered, washed with pentane, and residual solvent was removed under vacuum to give **2** (54 mg, 73%). Crystallization was accomplished by slow cooling of a toluene solution of **2**. ^{1}H NMR ($CDCl_3$): δ = 8.62 (d, J = 5.9 Hz, 2 H), 7.20 (d, J = 5.9 Hz, 2 H), 4.39 (dd, J = 11.3, 4.8 Hz, 2 H), 4.29 (t, J = 10.4 Hz, 2 H), 3.40 (m, 1 H) ppm. ^{13}C NMR: not recorded due to low solubility. ^{11}B NMR ($CDCl_3$): δ = 18.5 ppm. $C_{14}H_9BF_5NO_2 \cdot 0.5C_7H_8$ (375.1): calcd. C 56.04, H 3.49, N 3.73; found C 56.19, H 3.45, N 3.96.

Compound 3: A mixture of 2-(4-pyridyl)propan-1,3-diol (34.5 mg, 225 μmol) and [3,5-bis(trifluoromethyl)phenyl]boronic acid (58.0 mg, 225 μmol) in toluene (45 mL) was heated under reflux conditions with a Dean Stark apparatus for 3 h. After this time, the mixture was allowed to cool to room temperature, the solvent was reduced to <5 mL, and pentane (10 mL) was added to induce precipitation of the product. The product was filtered, washed with pentane, and residual solvent was removed under vacuum to give **3** as an off-white solid (52 mg, 62%). Crystallization was accomplished by slow diffusion of pentane into a concentrated solution of **3** in chloroform. ^{1}H NMR ($CDCl_3$): δ = 8.65 (dd, J = 4.5, 1.6 Hz, 2 H), 8.26 (s, 2 H), 7.96 (s, 1 H), 7.22 (dd, J = 4.5, 1.6 Hz, 2 H), 4.42 (dd, J = 11.2, 4.8 Hz, 2 H), 4.30 (t, J = 10.6 Hz, 2 H), 3.38 (m, 1 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 150.4, 145.9, 133.8 (br. s), 130.8 (q, J = 33.0 Hz), 124.4 (m), 123.6 (q, J = 272.6 Hz), 122.9, 66.0, 42.2 (B–C was not observed) ppm. ^{19}F NMR ($CDCl_3$): δ = –62.9 ppm. ^{11}B NMR ($CDCl_3$): δ = 26.7 ppm. $C_{19}H_{10}BF_6NO_2$ (409.09): calcd. C 51.24, H 3.22, N 3.73; found C 51.52, H 3.14, N 3.95.

4-(3-Pyridyl)catechol: The ligand was synthesized by modification of a published procedure.[15] A mixture of 4-bromoveratrole (0.48 mL, 3.3 mmol), (3-pyridinyl)boronic acid (525 mg, 4.3 mmol), $[Pd(PPh_3)_4]$ (248 mg, 0.21 mmol), and Na_2CO_3 (3.5 g, 33 mmol) in H_2O/dioxane (1:1, 60 mL) was heated under reflux conditions for 1 h. Water (60 mL) and Et_2O (60 mL) were added to the reaction mixture, the organic layer was separated, and the water phase was extracted with Et_2O (60 mL) twice. The combined organic phase was washed with water (20 mL), brine (20 mL), and then dried with $MgSO_4$. The solution was concentrated to approximately 1 mL, and the residue was purified by chromatography (CH_2Cl_2/Et_2O = 4:1) to give a light yellow oil, which was dissolved in HBr solution (47%, 30 mL) and heated to reflux for 3 h. The solution was cooled, and the white precipitate was filtered, washed with acetone, and then dried under vacuum to give 4-(3-pyridyl)catechol hydrogen bromide salt (352 mg, 1.2 mmol, 39.8%). ^{1}H NMR (CD_3OD): δ = 9.07 (s, 1 H), 8.83 (d, J = 8 Hz, 1 H), 8.73 (d, J = 6 Hz, 1 H), 8.12 (m, 1 H), 7.26 (d, J = 2.4 Hz, 1 H), 7.22 (d, J = 2.4 Hz, 1 H), 7.20 (d, J = 2.0 Hz, 1 H), 6.99 (d, J = 8 Hz, 1 H) ppm.

Compound 4: A mixture of 4-(3-pyridyl)catechol hydrobromide salt (60.3 mg, 225 μmol) and silver acetate (37.6 mg, 225 μmol) in methanol (6 mL) was stirred for 10 min before filtration. The solution was dried by vacuum before toluene (45 mL) and [3,5-bis(trifluoromethyl)phenyl]boronic acid (58.0 mg, 225 μmol) were added. The mixture was heated under reflux conditions with a Dean Stark apparatus for 3 h. After this time, the mixture was filtered hot and allowed to cool to room temp. The solvent was reduced to <5 mL, and pentane (10 mL) was added to induce precipitation of the product. The product was filtered, washed with pentane, and residual solvent was removed under vacuum to give **4** as a yellow solid (31 mg, 35%). Crystallization was accomplished by slow diffusion of pentane into a concentrated solution of **4** in benzene. NMR spectroscopic measurements gave a mixture of trimer/tetramer in a 1:1.22 ratio at a monomer concentration of 10 mM. ^{1}H NMR ($CDCl_3$): δ = 9.04 (s, 1 H_{trimer}), 8.97 (s, 1 $H_{tetramer}$), 8.61 (s, 1 $H_{tetramer}$), 8.26–8.22 (m, 2 H_{trimer}, 1 $H_{tetramer}$), 8.10 (s, 2 H_{trimer}), 8.05 (s, 2 $H_{tetramer}$), 7.83 (s, 1 H_{trimer}), 7.75 (s, 1 $H_{tetramer}$), 7.71–

Table 1. Selected crystallographic data for **1**–**4**.[a]

	1	**2**·0.5 toluene	**3**·2 $CHCl_3$	**4**·1 benzene
Empirical formula	$C_{18}H_{22}BNO_2$	$C_{17.50}H_{13}BF_5NO_2$	$C_{18}H_{14}BCl_6F_6NO_2$	$C_{63}H_{36}B_3F_{18}N_3O_6$
M_r	295.18	375.10	613.81	1305.38
T [K]	100(2)	140(2)	100(2)	140(2)
λ [Å]	0.71073	0.71073	0.71073	0.71073
Crystal system	orthorhombic	triclinic	monoclinic	monoclinic
Space group	*Pnma*	$P\bar{1}$	$P2_1/n$	$P2_1/n$
a [Å]	10.8803(11)	7.3754(7)	11.1284(16)	18.7601(10)
b [Å]	9.5482(5)	10.3702(13)	17.939(3)	13.2475(9)
c [Å]	15.9052(17)	11.4243(12)	13.200(2)	27.5549(14)
α [°]	90	63.978(12)	90	90
β [°]	90	83.985(8)	107.277(12)	90.546(5)
γ [°]	90	76.040(10)	90	90
V [Å^3]	1652.3(3)	762.01(15)	2516.3(7)	6847.8(7)
Z	4	2	4	4
$D_{calcd.}$ [Mg m^{-3}]	1.187	1.635	1.620	1.266
μ [mm^{-1}]	0.076	0.146	0.745	0.114
F(000)	632	382	1224	2640
Crystal size [mm^3]	0.46 × 0.38 × 0.32	0.22 × 0.20 × 0.15	0.23 × 0.22 × 0.20	0.28 × 0.19 × 0.13
θ range [°]	3.75 to 27.52	2.85 to 27.31	3.07 to 25.32	2.90 to 27.56
Index ranges	$-14 \le h \le 14$, $-12 \le k \le 12$, $-20 \le l \le 20$	$-9 \le h \le 9$, $-13 \le k \le 13$, $-14 \le l \le 14$	$-13 \le h \le 13$, $-21 \le k \le 21$, $-15 \le l \le 15$	$-23 \le h \le 23$, $-16 \le k \le 17$, $-35 \le l \le 34$
Reflections collected	3415	4951	26971	61111
Independent reflections	2007 [R(int) = 0.0321]	4951 [R(int) = 0.0000]	4563 [R(int) = 0.0938]	14548 [R(int) = 0.1092]
Completeness to θ [%]	99.7	99.1	99.5	99.6
Max./min. transmission	1.0000/0.8774	1.00000/0.65145	0.7452/0.6065	1.00000/0.94340
Data/restraints/parameters	2007/0/168	4951/0/272	4563/72/335	14548/324/951
GoF on F^2	1.067	0.986	1.152	0.730
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0441, $wR2$ = 0.1067	$R1$ = 0.0566, $wR2$ = 0.1434	$R1$ = 0.1045, $wR2$ = 0.2171	$R1$ = 0.0497, $wR2$ = 0.0948
R indices (all data)	$R1$ = 0.0546, $wR2$ = 0.1162	$R1$ = 0.0770, $wR2$ = 0.1531	$R1$ = 0.1691, $wR2$ = 0.2446	$R1$ = 0.1833, $wR2$ = 0.1147
Largest diff. peak/hole [e Å^{-3}]	0.359/–0.233	0.320/–0.281	0.647/–0.588	–

[a] For all compounds, the absorption correction method used was semiempirical from equivalents and the refinement method was full-matrix least-squares cycles on F^2.

7.66 (m, 1 H_{trimer}, 1 $H_{tetramer}$), 7.21–6.96 (m, 3 H_{trimer}, 3 $H_{tetramer}$) ppm. ^{13}C NMR ($CDCl_3$): δ = 153.3, 152.5, 141.2–139.6 (m), 131.7–130.3 (m), 126.2, 123.8 (q, J = 272.7 Hz), 121.8, 111.1, 108.9 (B–C was not observed) ppm. ^{19}F NMR ($CDCl_3$): δ = –62.59 (s, 6 F), –62.61 (s, 6 F) ppm. ^{11}B NMR ($CDCl_3$): δ = 10.2 ppm. $C_{19}H_{10}BF_6NO_2$ (409.08): calcd. C 55.78, H 2.46, N 3.42; found C 56.42, H 2.44, N 3.52.

Compound 5: Compound **5** (57 mg, 0.30 mmol) was synthesized as described for **4** by using [4-(trifluoromethyl)phenyl]boronic acid; yield 71 mg, 0.21 mmol, 70%. ^1H NMR ($CDCl_3$): δ = 9.00 (s, 1 H), 8.44 (br., 1 H), 8.19 (d, J = 8.0 Hz, 1 H), 7.23 (m, 2 H), 7.65 (m, 1 H), 7.59 (m, 2 H), 7.10 (s, 1 H), 6.97 (s, 2 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 153.7, 152.8, 141.1, 139.5, 131.9, 126.0, 124.6, 123.3, 119.6, 111.1, 108.9 (B–C was not observed) ppm. ^{19}F NMR ($CDCl_3$): δ = –62.58 ppm. ^{11}B NMR ($CDCl_3$): δ = 14.7 ppm. $C_{18}H_{11}BF_3NO_2$ (341.09): calcd. C 63.38, H 3.25, N 4.11; found C 63.07, H 3.33, N 3.95.

Compound 6: Compound **6** (32 mg, 0.23 mmol) was synthesized as described for **4** using (4-fluorophenyl)boronic acid; yield 30 mg, 0.10 mmol, 43%. ^1H NMR ($CDCl_3$): δ = 8.97 (s, 1 H), 8.50 (d, J = 5.2 Hz, 1 H), 8.14 (d, J = 8.0 Hz, 1 H), 7.59 (m, 3 H), 6.97–7.10 (m, 5 H) ppm. ^{13}C NMR: not recorded due to low solubility. ^{19}F NMR ($CDCl_3$): δ = –113.6 ppm. ^{11}B NMR ($CDCl_3$): δ = 15.6 ppm. $C_{17}H_{11}BFNO_2$ (291.09): calcd. C 70.15, H 3.81, N 4.81; found C 70.05, H 4.01, N 4.42.

Crystallographic Analyses: Intensity data for **2** and **4** were collected with an Oxford Diffraction KM-4 CCD diffractometer, whereas a Bruker APEX II CCD was employed in the case of **1** and **3**, both of which have kappa geometry, and graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) at low temperature was used. A summary of the crystallographic data, the data collection parameters, and the refinement parameters are given in Table 1. Data reduction was carried out with CrysAlis PRO[16] (**2** and **4**) and EvalCCD[17] (**1** and **3**) and then corrected for absorption.[18] Structure solution and refinement were performed with the SHELXTL software package.[18] The structures were refined using the full-matrix least-squares cycles on F^2. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included to the models in calculated positions using the riding model.

CCDC-915017 (for **3**), -915018 (for **2**), -915019 (for **1**), and -915020 (for **4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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