Self-assembled cyclic boron-dipyrrin oligomers†

Chusaku Ikeda and Tatsuya Nabeshima*

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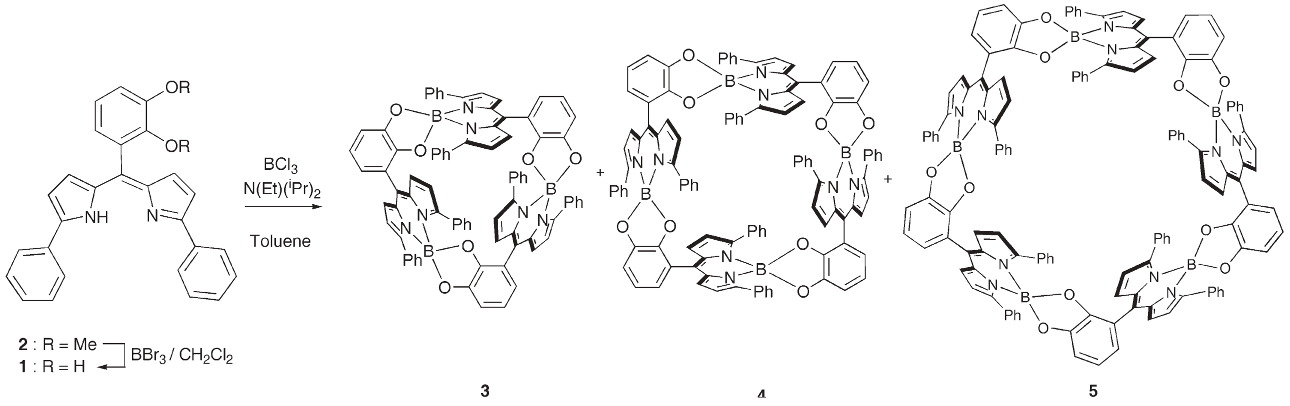
Self-assembled cyclic boron–dipyrrin oligomers 3–5 obtained by the reaction of catecholyldipyrrin with boron trichloride were characterized by ^{1}H NMR, MALDI-TOF MS, and X-ray measurements and the interaction between 3 and alkali metal ions was examined.

Construction of a nano-coordination space that has different properties compared to those of the outer environment is one of the most active topics in supramolecular chemistry and material science.[1] The utilization of metal-directed self-assembly is one of the most versatile and efficient ways to construct such a nanospace because the self-assembly of simple organic ligands can afford an elaborate capsule or cage. These systems are of particular interest because of their ability to encapsulate guest(s) with a high selectivity[2a] and to provide a space for specific reactions.[2b,c] Dipyrrin (dipyrromethene) is a suitable ligand for self-assembly because of its interesting optical properties, facile coordination with various metal ions, and easy synthetic accessibility. Due to the fully conjugated planar bipyrrolic structure, the dipyrrin complex has a large absorption in the visible range. Some of the dipyrrin complexes, especially those of the boron complexes, such as 4,4-difluoro-4-bora-3a,4a-diaza-*S*-indacene (BODIPY) dye, are strongly fluorescent.[3] Dipyrrin reacts with a suitable divalent or trivalent metal ions to give bis- or tris-dipyrrinato metal complexes which have no counter ion because dipyrrin works as a bidentate mono-anionic ligand. In addition, the complexes can often be purified by common chromatography methods. These valuable properties have stimulated considerable interest to create various supramolecular structures such as a helicate and cyclic assembly,[4] a metal–organic framework,[5] and a nanoscale aggregate,[6] which are constructed by utilizing the transition metal complexes of the dipyrrin derivatives. However, a discrete oligomeric boron–dipyrrin complex with a cavity as a guest binding site has not been reported.

We now report the cyclic assembly of boron–dipyrrin complexes that is able to recognize a cationic guest in the cavity. We have introduced a catecholyl group into the dipyrrin unit because the boron complexation between the catecholyl moiety and the dipyrrinato moiety would afford a versatile self-assembled complex arranged in a head-to-tail fashion. The properties and functions of the assembly could be easily controlled by changing the catecholyl moiety.

Dipyrrin **1** was prepared from the catechol-OH protected precursor **2** which was synthesized *via* the acid catalyzed condensation of 2-phenylpyrrole and 2,3-dimethoxybenzaldehyde followed by oxidation. The reaction of **1** with BCl_3 in refluxing toluene gave an oligomeric mixture, which was chromatographed on silica-gel. Gel permeation chromatography then gave **3**, **4** and **5** in 2%, 5%, and 0.3% yields, respectively. **3**, **4** and **5** are soluble in the common organic solvents such as chloroform, benzene, and ethyl acetate.

The formations of the self-assembled oligomers were first suggested by the MALDI-TOF mass spectrum. Strong peaks were observed at *m*/*z* 1237.2 (for **3**), 1649.3 (for **4**), and 2062.6 (for **5**), which corresponded to a M + H$^+$ peak of the self-assembled trimer (MW = 1236.41), tetramer (MW = 1648.55), and pentamer (MW = 2061.24) of the boron complexes of **1** (Scheme 1). In all the



Scheme 1 Synthetic scheme of cyclic oligomers.

Graduate School of Pure and Applied Sciences, University of Tsukuba, Tsukuba, Ibaraki, 305-8571, Japan.
E-mail: nabesima@chem.tsukuba.ac.jp; Fax: +81-29-853-4507; Tel: +81-29-853-4507

† Electronic supplementary information (ESI) available: Synthetic procedure and spectral data of **3–5**, algorithm for competition experiment, and the calculated structures of **3** with guest cations. See DOI: 10.1039/b716453j

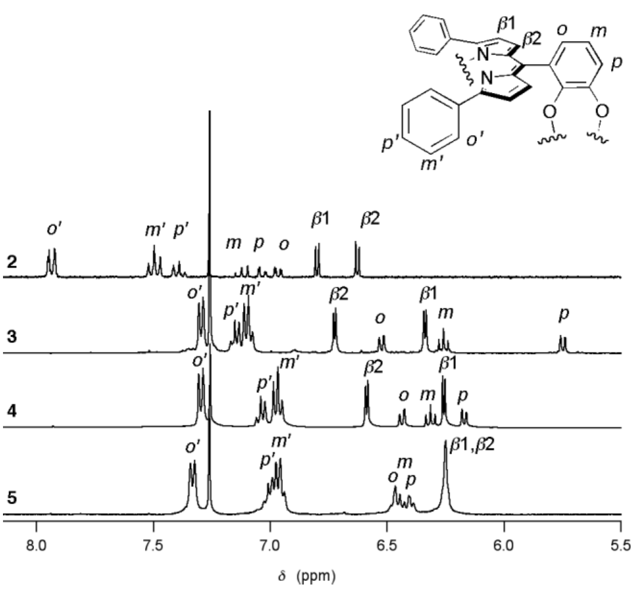


Fig. 1 ^{1}H NMR spectra of **2**, **3**, **4**, and **5** recorded in $CDCl_3$.

spectra, neither decomposed peaks nor fragmented peaks were observed.

The ^{1}H NMR spectra of **3–5** suggested the cyclic structures, because **3**, **4** and **5** showed a single set of proton resonances for the single dipyrrin unit (Fig. 1). The H_p and H_m of **3–5** also appeared in a higher field compared to those of the monomer **2**. These shifts are well rationalized by the ring current effect of the phenyl rings because the catechol rings are "sandwiched" by two phenyl rings upon coordination with boron. Furthermore, the head-to-tail arrangement of the self-assembly was supported by the ROE correlations of $H_{p'}$ with $H_{\beta1}$and $H_{\beta2}$ observed for **3** and **4**.

The ^{11}B NMR showed a broad singlet at 7.58, 7.51, and 7.64 ppm for **3**, **4**, and **5**, respectively, reflecting the tetrahedral boron complex with an N_2O_2 ligand.[7] These facts suggest that discrete cyclic oligomers **3–5** are formed in chloroform solution.

The X-ray crystal crystallographic analysis showed that **3** and **4** have triangular- and square-prism structures composed of the dipyrrins, which are connected by the boron atom coordinated to the two pyrrolic nitrogens and the two catecholate oxygen atoms (Fig. 2).‡§ The tetrahedral geometry of the central boron in **3** and **4** is slightly distorted. The average bond angles of O–B–O, N–B–N, and O–B–N are 106.0°, 105.8°, and 111.2° for **3** and 105.4°, 106.2°, and 111.4° for **4**, respectively. In **3**, the catechol moieties lie almost perpendicular (87°) to the dipyrrin plane, and the boron centers slightly deviate from each dipyrrin plane (0.33 Å on average) towards the inside of the triangular cavity. As a result, the dihedral angle between the planes containing the N–B–N atoms and the dipyrrolic planes averages 21.3°, which may be suitable to afford a cyclic trimer. In the case of **4**, the tilting angle of the catechol ring was 60.7°, resulting in a slightly distorted square prism structure. In both cases, the inner catecholyl oxygens form cavities with a radius of *ca.* 1.4 Å and 2.7 Å for **3** and **4**, respectively.

Additionally, the square-prism assemblies of **4** stacked along the crystallographic *c*-axis form one-dimensional channels filled with solvent molecules. The observed channel structure may be interesting in view of the nano-porous materials based on the discrete cyclic complexes (Fig. 3).[8]

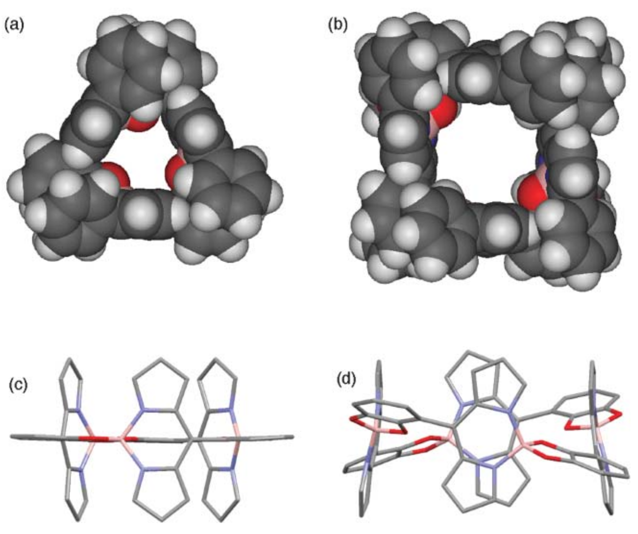


Fig. 2 Crystal structures of **3** (a, c) and **4** (b, d). Parts (a) and (b) show top views with the space-filling representation and (c) and (d) show side views with a stick framework. One of the structures of **4** is shown in (b) and (d) out of two molecules in the asymmetric unit. Color: C gray, H white, B pink, N blue, O red. The phenyl groups and hydrogen atoms in (c) and (d) as well as the solvent molecules are omitted for clarity.

Since **3** has a cavity (*ca.* 3 Å) surrounded by catecholate oxygens as well as electron-rich pyrrolic planes, the interaction of **3** with alkali-metal ions was examined in $CDCl_3 : CD_3OD$ (9 : 1) by ^{1}H NMR spectroscopy.[9] **3** showed no interaction with Na^+ because no spectral change was observed by the Na^+ ion. This is presumably because the ionic radius of Na^+ (0.97 Å)[10] is smaller than the cavity radius (1.4 Å) of **3**. In contrast, K^+, Rb^+, and Cs^+ caused considerable spectral changes. The ^{1}H NMR titration indicated the formation of the 1 : 1 complexes.

The K_a value for K^+ was determined to be $(1.5 \pm 0.6) \times 10^4\ M^{-1}$ by analyzing the titration isotherms using a nonlinear-least-squares regression. The K_a values for Rb^+ and Cs^+ were estimated to be at least $5.7 \times 10^4\ M^{-1}$ and $5.5 \times 10^6\ M^{-1}$, respectively, based on the competition experiment with the K^+ ion. In the case of Cs^+, which has a larger ionic radius (1.67 Å)[10] than the cavity radius (1.4 Å), an upfield shift of the pyrrole-β_1 protons

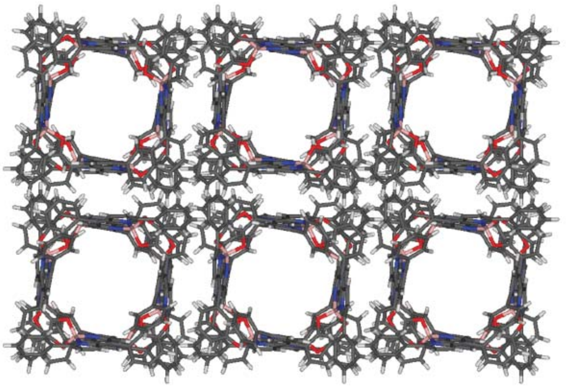


Fig. 3 Stick framework projection showing the packing arrangement of square **4** viewed down the crystallographic *c*-axis. Solvent molecules have been omitted for clarity.

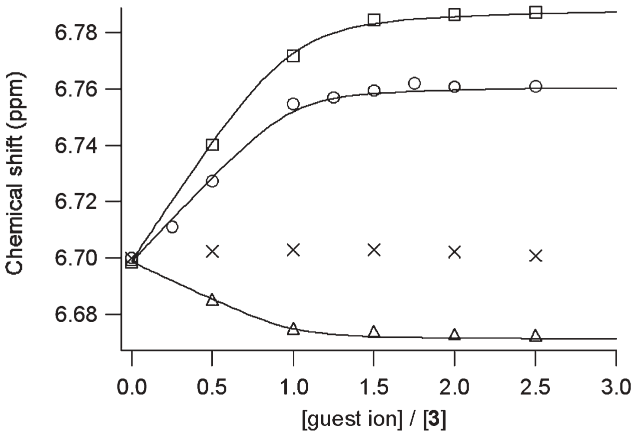


Fig. 4 Changes in the chemical shift upon the addition of the guest ions. Guest = K^+ (square), Rb^+ (circle), Na^+ (crosses), and Cs^+ (triangle). The solid lines are the calculated binding curves.

was observed, whereas K^+ and Rb^+ caused downfield shifts (Fig. 4).

This result may be ascribed to the different coordination geometry of the cations. The Hartree–Fock calculation suggested that Cs^+ locates above the central O3 cavity stabilized by coordination with the oxygen atoms as well as the cation–π interaction with the pyrrolic rings, whereas K^+ fits well within the cavity *via* effective interactions with the three oxygen atoms but without the cation–π interactions (see Fig. S6†).

In conclusion, we have synthesized the novel cyclic self-assemblies **3**, **4** and **5** *via* boron–dipyrrin complexation. The ^1H NMR titration studies suggested that **3** is used as a supramolecular host with a binding site surrounded by the oxygen atoms. A detailed investigation of the recognition ability of **3**, **4** and **5** with various guest ions or guest molecules is now in progress.

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Notes and references

‡ The crystal of **4** contains two independent molecures of **4** both with S_4 symmetry.

§ Crystal data for **3**·2CHCl$_3$·2CH$_3$CN: $C_{87}H_{59}B_3Cl_6N_8O_6$, M = 1557.55, monoclinic, a = 14.025(3), b = 23.337(6), c = 22.624(5) Å, β = 90.068(8), U = 7405(3)Å^3, T = 120 K, space group Cc (no. 9), Z = 4, 36155 reflections measured, 15623 unique (R_{int} = 0.0315). $R1 = 0.0621(I > 2\sigma(I))$,w$R2$ = 0.1740 (all data), GOF (F^2) = 1.046. Fack χ parameter = 0.03(5), 7149 Friedel pairs were used in the refinement.[11]

Crystal data for **4**·2CH$_3$CO$_2$C$_2$H$_5$·4C$_6$H$_6$: $C_{140}H_{108}B_4N_8O_{12}$, M = 2137.58, tetragonal, b = 27.870(5), c = 28.442(6) Å, U = 22092(8)Å^3, T = 120 K, space group $I4_1/a$ (no. 88), Z = 8, 78962 reflections measured, 9697 unique (R_{int} = 0.1126). $R1 = 0.1038$ ($I > 2\sigma(I)$), w$R2$ = 0.3182 (all data), GOF (F^2) = 1.033.[11]

CCDC 665385 & 665386. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b716453j

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