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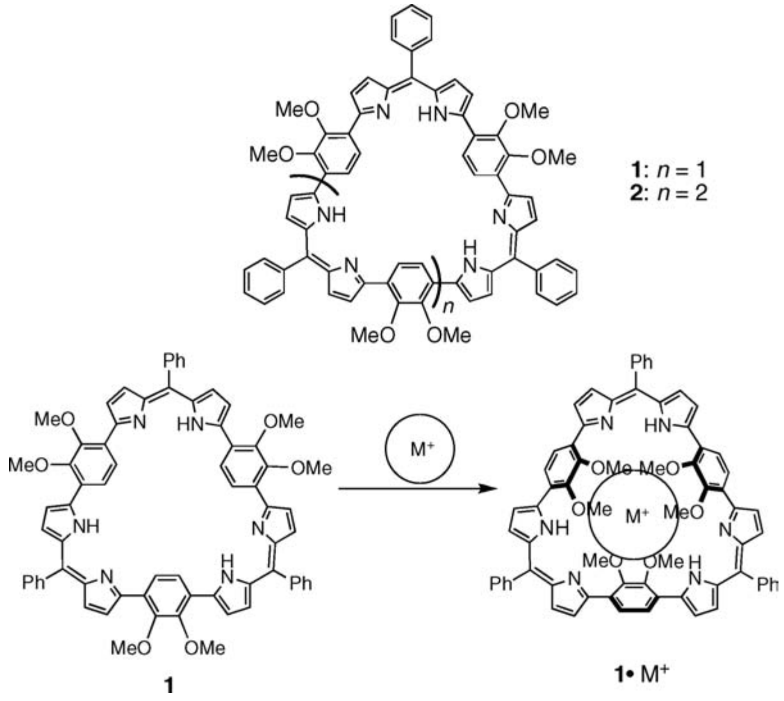

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Synthesis and Guest Recognition Ability of 2,3-Dimethoxy-1,4-phenylene-Containing Porphyrinoids

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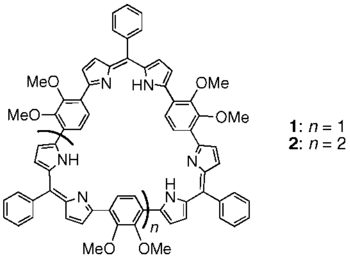
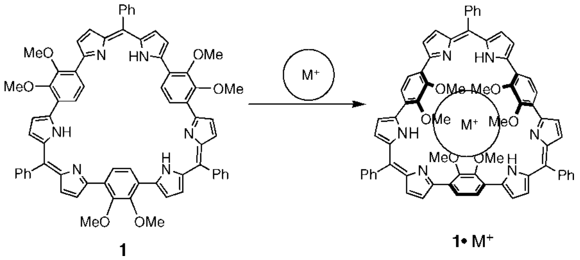
ABSTRACT





The acid-catalyzed condensation of the bispyrrolylbenzene derivative and benzaldehyde yielded macrocycles 1 and 2 bearing three and four dipyrrin units which are connected by 2,3-dimethoxy-1,4-phenylene rings. The cationic guest recognition ability of 1 was investigated by UV−vis absorption, ^{1}H NMR spectroscopic techniques, and ab initio calculations (HF/3-21G(*)). The tris-dipyrrin macrocycle 1 was found to recognize alkali metals in the O_6 binding cavity.

Conjugated macrocycles have attracted significant attention in recent years due to their distinctive physical properties and potential applications. Among the various macrocycles, the conjugated oligopyrrolic ones, such as the expanded porphyrins,[1] are particularly interesting because the conjugation along the macrocyclic skeleton can be changed by a redox reaction,[2] protonation,[3] conformational change,[4] or metal complexation.[5] If the conjugation structure of the macrocycle can be modulated by external stimuli such as a guest, it would lead to an interesting supramolecular host, which shows a drastic change in the properties based on a change in the conjugation upon guest binding. To date, the recognition of an anion,[6] alcohol,[7] and carboxylic acid[8] has been achieved by the porphyrinoids, and the changes in the conjugation structure were shown in some cases.

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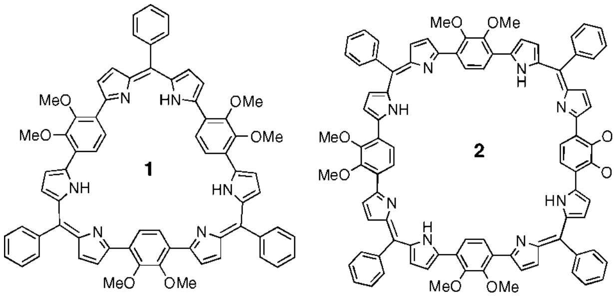
As another class of porphyrinoids, novel macrocycles containing nonpyrrolic bridging groups have been reported, and the effective binding with the anion[9] and carboxylic acid[10] has been accomplished. However, the macrocyclic conjugation is often interrupted by the nonpyrrolic bridging groups.

Among the various bridging groups, the 1,4-phenylene ring is highly attractive because the phenylene ring is known to contribute to the macrocyclic conjugation depending on the tilting angle with the neighboring aromatic rings.[4,11] Furthermore, various substituents that bind guests can be introduced into the phenylene ring.

We reported the synthesis of macrocyclic polyimine ligands containing 2,3-dihydroxy-1,4-phenylene moieties.[12,13] The metal complexes of these ligands recognize other cationic guests in the O_6 binding site in the cavity.[13,14] In this context, we have synthesized the oligopyrrole macrocycles **1** and **2**[15] containing 2,3-dimethoxy-1,4-phenylene linkages because the guest recognition using the oxygen atoms may tilt the phenylene rings and thus induce a change in the optical properties based on the conjugation structure (Scheme 1).

Scheme 1. Structures of Macrocycles **1** and **2**



This paper describes the recognition of cationic guests by the oligopyrrole macrocycle **1** and the large bathochromic shift upon guest binding. We also examined the structures of **1** and **2** by ^1H NMR spectroscopy and X-ray crystallography to clarify the effect of the conformation and the rotation freedom of the phenylene moieties on the guest binding properties.

Macrocycles **1** and **2** were synthesized via the acid-catalyzed condensation of 1,4-bis(2-pyrrolyl)-2,3-dimethoxybenzene and benzaldehyde followed by oxidation with DDQ. Purification by silica gel chromatography and gel permeation chromatography gave **1** and **2** in 24% and 1.5% yields, respectively.

In the ^1H NMR spectra of **1** and **2**, the pyrrolic-β protons appeared as two sets of doublets at 6.48 and 6.72 ppm for **1** and 6.69 and 6.97 ppm for **2**. These chemical shifts are roughly the same as those of the corresponding dipyrrin monomer, 1,9-bis(2,3-dimethoxyphenyl)-5-phenyldipyrrin **5** ($\delta_{\beta\text{-pyrrole}} = 6.65$ and 7.00 ppm, see Figure S1, Supporting Information). These results showed that the macrocyclic conjugation of **1** and **2** is negligibly small. The methoxy protons and aryl protons of the phenylene rings of **1** and **2** were observed as a sharp singlet at room temperature but broadened by lowering the temperature to 188 K. This result shows that the flipping of the phenylene rings is fast on the NMR time scale at room temperature.

The crystallographic analysis of **1** revealed a planar triangle structure, in which the six pyrrole rings are nearly coplanar with the maximum mean plane deviation of 0.421 Å (Figure 1).[16] The three dimethoxyphenylene rings are tilted with respect to the six-pyrrolic plane with tilting angles of 18°, 0.8°, and 144°

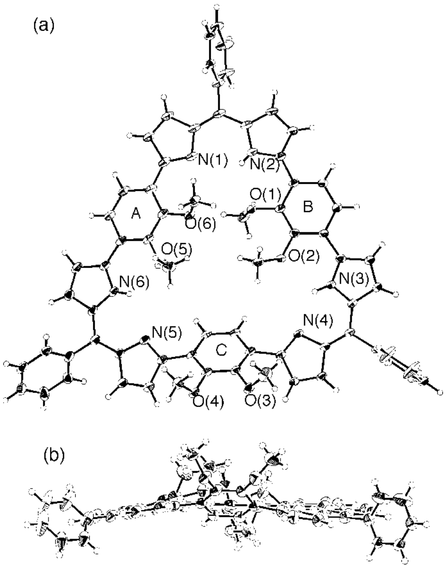


Figure 1. Crystal structure of of **1**·3.5$CHCl_3$ (ORTEP, 50% probability). (a) and (b) show the top and side view, respectively. The solvent molecules are omitted for clarity.

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(15) (a) Ikeda, C.; Sakamoto, N.; Nabeshima, T. 12th International Symposium on Novel Aromatic Compounds, Awaji Island, Japan, 22−27 July, 2007, p 376. Very recently, the rhodium complex of the analogue to **1** was reported. See: (b) Setsune, J.; Toda, M.; Yoshida, T. *Chem. Commun.* **2008**, 1425.

(16) Crystallographic data for **1**·3.5$CHCl_3$: $C_{72.5}H_{57.5}Cl_{10.5}N_6O_6$, M = 1480.97, triclinic, a = 14.85(2) Å, b = 14.88(2) Å, c = 17.50(3) Å, α = 101.00(6)°, β = 108.81(7)°, γ = 104.85(6)°, U = 3376(9) Å^3, T = 120(2) K, space group P-1 (no. 2), Z = 2, 26847 reflections measured, 11868 unique ($R_{\text{int}} = 0.0549$). R1 = 0.1110 ($I > 2\sigma(I)$), wR2 = 0.2559 (all data), GOF (F^2) = 1.067.

for rings A, B, and C, respectively.[17] The tilted orientations of the phenylene rings forced the four methoxy groups inward and the other two groups outward.

On the other hand, the X-ray crystallographic study of **2** revealed a twisted figure-eight structure that is located on the crystallographic 2-fold axis (Figure 2).[18] The pyrrole rings E, F, and the dimethoxyphenylene ring D are nearly coplanar with a maximum mean plane deviation of 0.08 Å. But the A, B, and C rings are not coplanar. The dihedral angles between rings A and B, and B and C are 29.2° and 19.4°, respectively. These distortions form a large cleft structure with the N(3)−N(3)* distance of 10.19 Å.

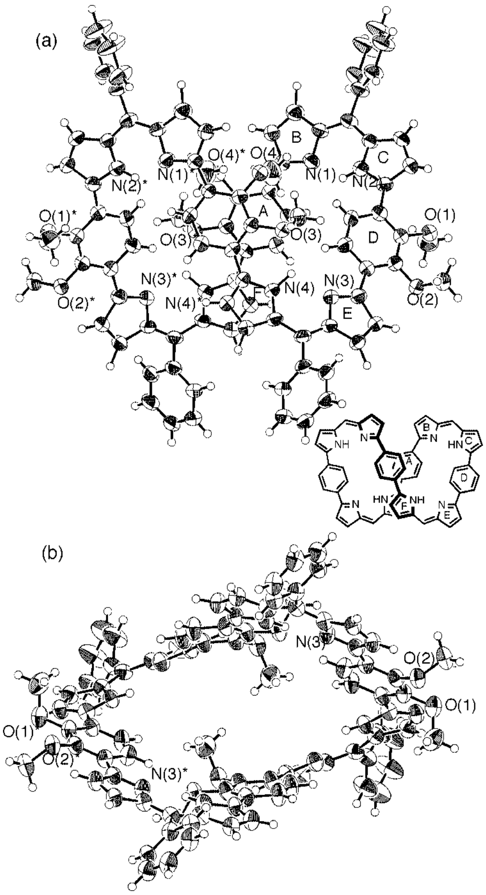

Figure 2. Crystal structure of **2**·$2CH_2Cl_2$ (ORTEP, 50% probability). (a) and (b) show the top and side views, respectively. Schematic view of (a) is also shown. The solvent molecules are omitted for clarity.

Since **1** has a rigid triangle framework with rotatable phenylene moieties bearing oxygen substituents, the interaction of **1** with alkali metal ions was examined by UV−vis spectroscopy. Figure 3 shows the changes in the UV−vis spectrum of **1** in toluene−acetonitrile (95:5) upon the addition of rubidium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (RbTFPB).

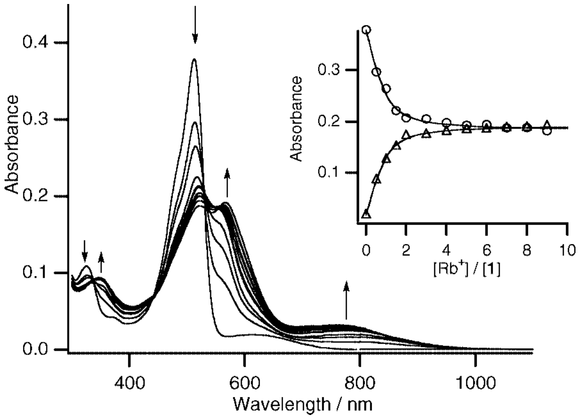

Figure 3. Absorption spectra of **1** (2.1 μM) recorded in toluene−acetonitrile (95:5) under various concentrations of RbTFPB. Inset shows the binding isotherm at 512 nm (circle) and 566 nm (triangle) analyzed by a nonlinear least-squares regression (calculated lines is shown in solid lines).

The addition of Rb^+ caused a decrease in the absorption intensity at 512 nm along with a concomitant increase in the absorption at 566 nm. Notably, a smaller broad absorption band at 650 nm in the absence of the guest cation shifted to ca. 780 nm with increasing intensity by the addition of Rb^+. Compound **1** also showed the interaction with K^+ and Cs^+ since significant spectral changes are also observed (Figures S2 and S3, Supporting Information).

The bathochromic shifts observed in the peak at 512 nm were 56, 54, and ca. 50 nm[19] for K^+, Rb^+, and Cs^+, respectively. The observed large bathochromic shifts may be attributed to the elongation of the effective π-conjugation along the macrocycle due to the conformational change upon the complexation with the cationic guests. Analysis of the observed spectral changes by the nonlinear least-squares regression supported the 1:1 stoichiometry with the association constants (K_a) of $(2.1 \pm 0.2) \times 10^6$, $(2.3 \pm 0.2) \times 10^6$, and $(2.5 \pm 0.3) \times 10^6$ M^{-1} for K^+, Rb^+, and Cs^+, respectively.

The Hartree−Fock calculation suggested that all the methoxy groups face inside and the guest cation locates in the center of the triangle core, which is stabilized by a cation−dipole interaction between the guest cation and the six oxygen atoms (Figure 4 for Rb^+ guest). The calculation showed that **1** also adopts a suitable conformation with K^+ or Cs^+ by maintaining the coordination distances between the cation and methoxy oxygens by changing the tilting angles of the phenylene rings. The calculated average distances between the cation and

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(17) The tilting angle is defined as the angle between the six-pyrrolic plane and the dimethoxyphenylene ring. A 0° angle denotes the in-plane geometry of the phenylene ring with the two oxygen atoms located inside the cavity.

(18) Crystal data for **2**·$2CH_2Cl_2$: $C_{94}H_{76}Cl_4N_8O_8$, $M = 1587.43$, orthorhombic, $a = 22.06(3)$ Å, $b = 12.69(2)$ Å, $c = 29.55(4)$ Å, $U = 8275(21)$ Å^3, $T = 120(2)$ K, space group *Pbcn* (no. 60), $Z = 4$, 57643 reflections measured, 7268 unique ($R_{int} = 0.1178$). R1 = 0.0807 ($I > 2\sigma(I)$), wR2 = 0.2099 (all data), GOF (F^2) = 0.995.

(19) Appropriate value due to the broad peak shape. See Figure S3 in the Supporting Information.

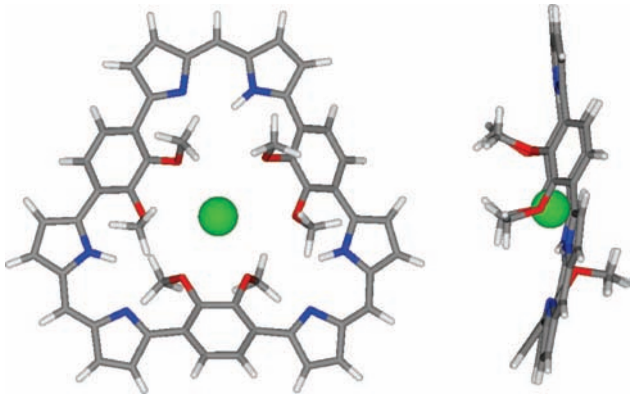

Figure 4. Proposed Rb^+-binding structure of **1** generated by Hartree−Fock calculations at the 3−21G (*) level. Calculation was carried out without the phenyl groups. Key: C, gray, H, white, N, blue, O, red, Rb, green.

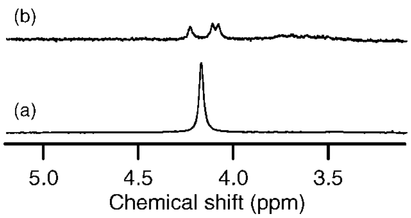

Figure 5. ^1H NMR spectra of (a) **1** and (b) **1** + RbTFPB recorded in toluene-d_8–CD_3CN (95:5) at room temperature. Concentrations of **1** and Rb^+ in (b) are 0.1 and 0.4 mM, respectively.

oxygen atoms were 2.95, 3.04, and 3.22 Å for K^+, Rb^+, and Cs^+, respectively, and the average tilting angles of the phenylene rings are 32.4°, 34.5°, and 36.9° for K^+, Rb^+, and Cs^+, respectively. The small angles contribute to the bathochromic shifts of the absorption spectra upon cation binding probably due to a more efficient π-conjugation in the rigid conformation with the small tilting angles between the aromatic rings than that of the flexible **1** in the absence of the cationic guest.

The expected conformational change was further supported by the ^1H NMR spectra of **1** in toluene-d_8–CD_3CN (95:5) (Figure 5). The methoxy protons of **1** appeared as a singlet at 4.17 ppm in the absence of the guest cations. However, the protons appeared as three singlets at 4.08, 4.11, and 4.23 ppm in the presence of 4 equiv of Rb^+. This result indicates that the flipping of the dimethoxyphenylene rings are suppressed on the ^1H NMR time scale by the interaction with Rb^+. The three singlets also agreed with the expected C_s symmetry of the proposed cation-binding structure.

In summary, novel macrocyclic hosts containing the dipyrrin moieties were synthesized from the bis-pyrrolylbenzene derivative. The spectroscopic studies and ab initio calculation suggested that the conjugation along the macrocycle **1** is changed by the recognition of the alkali metals in the cavity. The results obtained in this study may be useful to construct a supramolecular host that can drastically switch its conjugation upon guest binding. The synthesis and properties of the corresponding demethylated derivatives with different binding properties are the subject of the current study.

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Supporting Information Available: Synthetic procedure and spectral data of **1** and **2**, calculated structures with K^+ and Cs^+, and ^1H NMR of **1** in the presence of the guest cations. This material is available free of charge via the Internet at http://pubs.acs.org.

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