Supporting information

Self-assembled cyclic boron-dipyrrin oligomers

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Contents

1. General

All chemicals were reagent grade, and used without further purification. THF was purified by distillation from benzophenone ketyl under argon atmosphere before use. All reactions were performed under nitrogen atmosphere. Column chromatography was performed with Kanto Chemical silica gel 60 N (spherical, neutral) or Wako Chemical alumina (activated, about 200 mesh). Gel-permeation chromatography (GPC) was performed at room temperature using columns JAIGEL 2H-1H on a Japan Analytical Industry LC-908 recycling preparative HPLC system equipped with a variable-wavelength UV-vis detector. ^{1}H NMR spectra were recorded on a Bruker ARX400 spectrometer at 400 MHz, or a Bruker AC300 spectrometer at 300 MHz. ^{13}C NMR spectra were recorded on a Bruker ARX400 spectrometer at 100 MHz. In both NMR measurements, tetramethylsilane was used as an internal standard. ^{11}B NMR spectra were recorded on a Bruker ARX400 spectrometer at 128 MHz using boron trifluoride-diethyl etherate as an external standard. UV-Vis spectra were recorded on JASCO V-660 spectrophotometer. Mass spectra (ESI-TOF, positive mode) were recorded on an Applied Biosystems QStar Pulsar *i* spectrometer. MALDI-TOF spectra were recorded on a Bruker BIFLES III with dithranol as matrix. Elemental analyses were performed at Chemical Analysis Center, University of Tsukuba. Geometry optimizations of cation binding structure were performed with Sparrtan04 programs.[1]

2. Synthesis

5-(2,3-Dimethoxyphenyl)-1,9-diphenyldipyrrin (2)

To a stirred solution containing 2,3-dimethoxybenzaldehyde (0.84 g, 5.0 mmol) and 2-phenylpyrrole (1.4 g, 10 mmol) in CH_2Cl_2 (200 mL) was added trifluoroacetic acid (TFA) (0.12 mL, 1.5 mmol) under nitrogen atmosphere and the mixture was stirred for 2 h under dark. 2,3-Dichloro-5,6-dicyano- 1,4-benzoquinone (DDQ) (1.1 g, 5.0 mmol) was added and the resulting solution was stirred overnight. The reaction mixture was washed with saturated $NaHCO_3$ aqueous solution, dried over Na_2SO_4, and evaporated to small volume that was loaded directly on the short alumina column and eluted with CH_2Cl_2. The first red band was collected and purified again using short SiO_2 column eluted with CH_2Cl_2. Red fraction was collected, evaporated to dryness, and recrystallized from CH_2Cl_2/hexane to give **2** (1.3 g, 54%). ^{1}H NMR ($CDCl_3$, 300

MHz) δ 3.70(s, 3H), 3.95(s, 3H), 6.63(d, 2H, J = 4.4 Hz), 6.80(d, 2H, J = 4.4 Hz), 6.97(dd, 1H, J = 7.5 and 1.5 Hz), 7.03(dd, 1H, J = 8.7 and 1.5 Hz), 7.12(t, 1H, J = 8.1 Hz), 7.39(t, 2H, J = 7.5 Hz), 7.50(t, 4H, J = 7.5 Hz), 7.94(d, 4H, J = 7.8 Hz). ^{13}C NMR($CDCl_3$, 100 MHz) δ 55.9(CH_3), 61.4(CH_3), 112.7(CH), 115.5(CH), 123.1(CH), 123.9(CH), 126.1(CH), 128.7(CH), 129.0(CH), 129.4(CH), 131.2(C), 133.2(C), 135.4(C), 142.2(C), 147.55(C), 152.5(C), 154.1(C). Mass(ESI): Obsd. *m/z* 433.21[$(M+H)^+$]; Cald. for $C_{29}H_{25}N_2O_2$, 433.19. Anal. Cald. for $C_{29}H_{24}N_2O_2$: C, 80.53; H, 5.59; N, 6.48. Found C, 80.62; H, 5.77; N, 6.37.

5-(2,3-Dihydroxyphenyl)-1,9-diphenyldipyrrin (1)

To a stirred solution containing **2** (1.3 g, 3.0 mmol) in CH_2Cl_2 (50 mL) was added BBr_3 (1.4 mL, 15 mmol) at 0 ^oC under nitrogen atmosphere. The reaction mixture was stirred overnight allowing to warm up to room temperature before poured into ice-cooled methanol (ca. 200 mL). To the obtained mixture was added conc. HCl (ca. 5 mL) and refluxed 3 hrs. After cooled down, the mixture was neutralized with saturated $NaHCO_3$ aqueous solution and extracted with ethyl acetate. The organic layer was dried over Na_2SO_4, evaporated to dryness, and recrystallized from THF/hexane to give **1** (1.2 g, quant). ^{1}H NMR (DMSO-d_6, 400 MHz) δ 6.65(d, 2H, J = 4.3 Hz), 6.68 (dd, 1H, J = 7.5 and 1.6 Hz), 6.74(t, 1H, J = 7.8 Hz), 6.92 (dd, 1H, J = 7.8 and 1.6 Hz), 6.98 (d, 2H, J = 4.3 Hz), 7.44 (t, 2H, J = 7.4 Hz), 7.57 (t, 4H, J = 7.7 Hz), 7.96 (d, 4H, J = 7.9 Hz). ^{13}C NMR(DMSO-d_6, 100 MHz) δ 116.2(CH), 116.3(CH), 118.8(CH), 122.5(CH), 124.3(C), 126.2(CH), 129.5(CH), 129.8(CH), 129.9(CH), 133.0(C), 137.1(C), 142.1(C), 144.2(C), 145.6(C), 153.5(C). Mass(ESI) : Obsd. *m/z* 405.17[$(M+H)^+$]; Cald. for $C_{27}H_{21}N_2O_2$, 405.16. Anal. Cald. for $C_{27}H_{20}N_2O_2$•THF : C, 78.13; H, 5.92; N, 5.88. Found C, 78.40; H, 5.58; N, 5.83.

Synthetic procedure for oligomers 3, 4, and 5

3 and **4**

To a stirred solution containing **1** (1.2 g, 3.0 mmol) in toluene (300 mL), *N*-ethyldiisopropylamine (1.1 mL, 6.0 mmol) and boron trichloride (3.0 mL of 1M heptane solution, 3.0 mmol) were added successively under N_2. After 5 min, the reaction mixture was refluxed overnight. After being cooled, precipitate was removed

by suction and the filtrate was evaporated to dryness. The residue was chromatographed on a short SiO_2 column (4 × 4 cm) eluted with chloroform. The first red band was collected and concentrated under reduced pressure to afford mixture of the oligomers, from which **3**(23 mg, 2%) and **4**(72 mg, 5%) were isolated by GPC chromatography (detected by the absorbance at 413 nm, the second and third peak were collected) by recycling-separation technique.

3 ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.75(d, 1H, J = 7.6 Hz), 6.26(t, 1H, J = 7.6 Hz), 6.35(d, 2H, J = 4.2 Hz), 6.53(d, 1H, J = 7.6 Hz), 6.72(d, 2H, J = 4.2Hz), 7.08-7.16(m, 6H), 7.30(d, 4H, J = 7.3 Hz). ^{13}C NMR($CDCl_3$, 100 MHz) δ 110.4(CH), 114.3(C), 117.4(CH), 119.0(CH), 121.2(CH), 126.9(CH), 128.4(CH), 129.0(CH), 130.4(CH), 132.9(C), 137.3(C), 143.2(C), 149.3(C), 150.2(C), 159.7(C). ^{11}B NMR($CDCl_3$, 128 MHz) δ 7.58(br s). Mass(MALDI-TOF): Obsd. *m/z* 1237.2[$(M+H)^+$]; Cald. for $C_{81}H_{52}B_3N_6O_6$, 1237.4.

4 ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.17(d, 1H J = 7.6 Hz), 6.26(d, 2H, J = 4.2 Hz), 6.32(t, 1H, J = 7.6 Hz), 6.44(d, 1H, J = 7.6 Hz), 6.59(d, 2H, J = 4.2 Hz), 6.97(t, 4H, J = 7.3 Hz), 7.04(t, 2H, J = 7.3 Hz), 7.29(d, 4H, J = 7.3 Hz). ^{13}C NMR($CDCl_3$, 100 MHz) δ 111.6(CH), 114.9(C), 117.4(CH), 120.6(CH), 122.1(CH), 127.3(CH), 128.2(CH), 129.0(CH), 132.8(C), 132.9(CH), 136.1(C), 142.9(C), 150.6(C), 150.8(C), 159.0(C). ^{11}B NMR($CDCl_3$, 128 MHz) δ 7.51(br s). Mass(MALDI-TOF): Obsd. *m/z* 1649.3[$(M+H)]^+$; Cald. for $C_{108}H_{69}B_4N_8O_8$, 1649.5. Anal. Cald. for $C_{108}H_{68}B_4N_8O_8$•$CHCl_3$: C, 74.03; H, 3.93; N, 6.34. Found C, 73.86; H, 4.04; N, 6.31.

5

To a stirred solution containing **1** (1.8 g, 4.4 mmol) in toluene (140 mL), *N*-ethyldiisopropylamine (1.5 mL, 8.8 mmol) and boron trichloride (4.4 mL of 1M heptane solution, 4.4 mmol) were added successively under N_2. After 5 min, the reaction mixture was refluxed overnight. After being cooled, precipitate was removed by suction and the filtrate was evaporated to dryness. The residue was chromatographed on a short SiO_2 column (4 × 4 cm) eluted with chloroform. The first red band was collected and concentrated under reduced pressure to afford mixture of the oligomers, from which **5**(4.2 mg, 0.3%) were isolated by GPC chromatography (detected by the absorbance at 413 nm, the first peak was collected) by recycling-separation technique. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.25(br. s, 4H),

6.38-6.49(m, 3H), 6.93-7.03(m, 6H), 7.33(d, 4H, J = 7.3 Hz). ^{13}C NMR($CDCl_3$, 100 MHz) δ 111.9(CH), 115.31(C), 117.7(CH), 121.4(CH), 123.4(CH), 127.5(CH), 128.4(CH), 129.1(CH), 132.8(C), 133.3(CH), 136.3(C), 143.1(C), 150.4(C), 150.8(C), 159.2(C). ^{11}B NMR($CDCl_3$, 128 MHz) δ 7.64(br s). Mass(MALDI-TOF): Obsd. *m/z* 2062.6[$(M+H)^+$]; Cald. for $C_{135}H_{86}B_5N_{10}O_{10}$, 2062.2.

3. Algorithm for Competition Assay

Since the ^{1}H NMR titration experiment showed that the molar fraction of the host-guest complex exceed 0.8 for Rb^+ and Cs^+, K_a value for Rb^+ and Cs^+ were estimated by competition experiment.[2]

$$[H] + [G_1] \overset{K_1}{\leftrightarrows} [HG_1], \qquad [H] + [G_2] \overset{K_2}{\leftrightarrows} [HG_2]$$

When the total concentrations of the added guest is larger than that of the host **3**, the amount of free host is negligible in the presence of large enough K_1, K_2 ([H] = 0). The equilibrium equation can be rewritten as the following equation.

$$[HG_1] + [G_2] \overset{K_2/K_1}{\leftrightarrows} [HG_2] + [G_1]$$

$$K_2/K_1 = ([HG_2][G_1]) / ([HG_1][G_2]) \qquad (1)$$

[H] = concentration of free host **3**

$[HG_1]$ = concentration of the complexed host **3** with potassium cation.

$[G_1]$ = concentration of the free potassium cation.

$[HG_2]$ = concentration of the complexed host **3** with rubidium or cesium cation.

$[G_2]$ = concentration of the free rubidium or cesium cation.

For the observed chemical shift (δ_{obs}), molar fraction of HG_1 can be written as

$$f_1 = \frac{\delta_{obs} - \delta_{HG_2}}{\delta_{HG_1} - \delta_{HG_2}} \qquad (2)$$

δ_{HG_1} = chemical shift of the complexed host **3** with potassium cation

δ_{HG_2} = chemical shift of the complexed host **3** with rubidium or cesium cation

From the mass balance

$[G_2]_t = [G_2] + [HG_2]$,

$[G_2] = [G_2]_t - [H]_t(1-f_1)$ (3)

similarly, $[G_1] = [G_1]_t - [H]_t f_1$ (4)

$[G_2]_t$ = total concentrations of the added rubidium or cesium cation

$[G_1]_t$ = total concentrations of the added potassium cation

$[H]_t = [H] + [HG_1] + [HG_2]$

$$\frac{[HG_2]}{[HG_1]} = \frac{[H]_t - [HG_1]}{[HG_1]} = \frac{1 - f_1}{f_1} \quad (5)$$

$[H]_t$ = total concentrations of **3**

combining the equations (1), (3), (4) and (5)

$$K_2 = K_1\left(\frac{1 - f_1}{f_1}\right)\left(\frac{[G_1]_t - [H]_t f_1}{[G_2]_t - [H]_t(1 - f_1)}\right) \quad (6)$$

According to the equation (2) and (6), binding constant of **3** with Rb^+ or Cs^+ was calculated using the ^1H NMR spectral data of **3** containing 1 equivalent of M^+ (M^+ = Rb^+ or Cs^+) and 1 or 10 equivalents of K^+.

4. MALDI-TOF Mass spectra of 3, 4, and 5

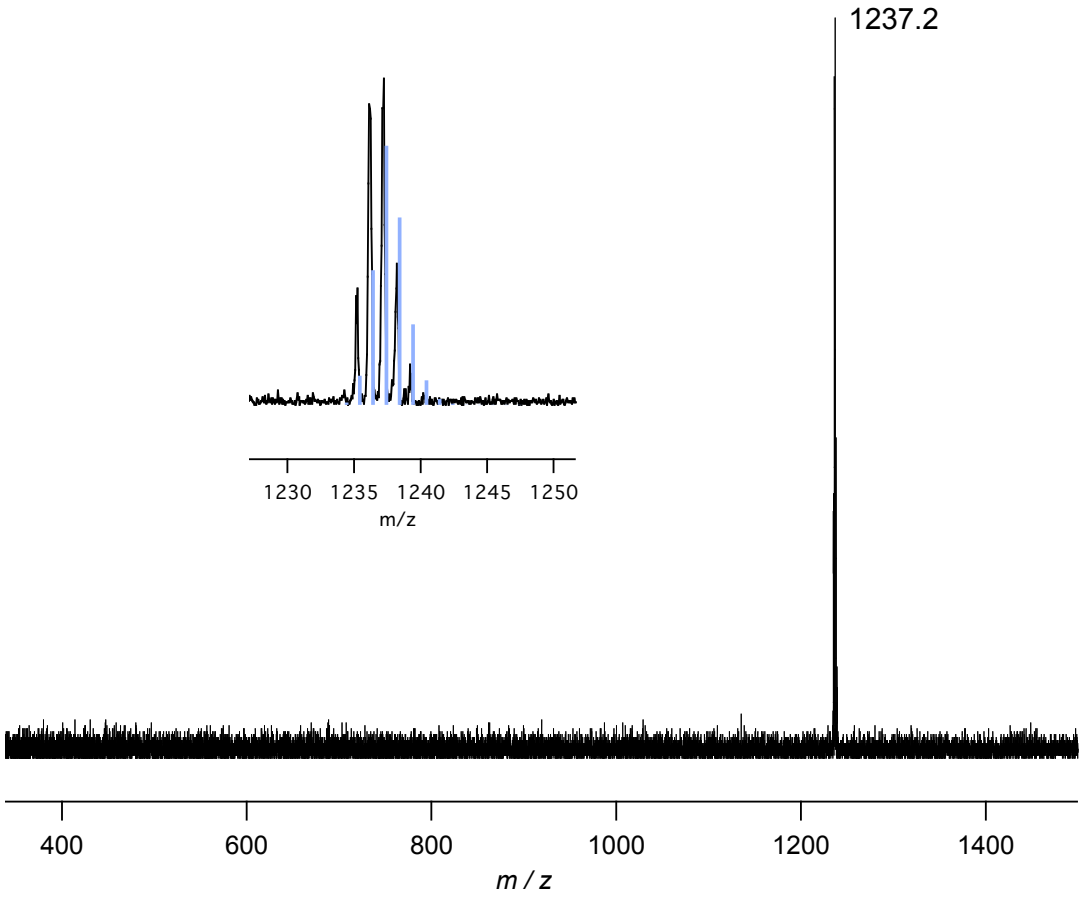

Fig. S1 MALDI-TOF mass spectrum of **3**. Insert shows the magnified spectrum (black line) and the calculated isotope pattern (blue bar).

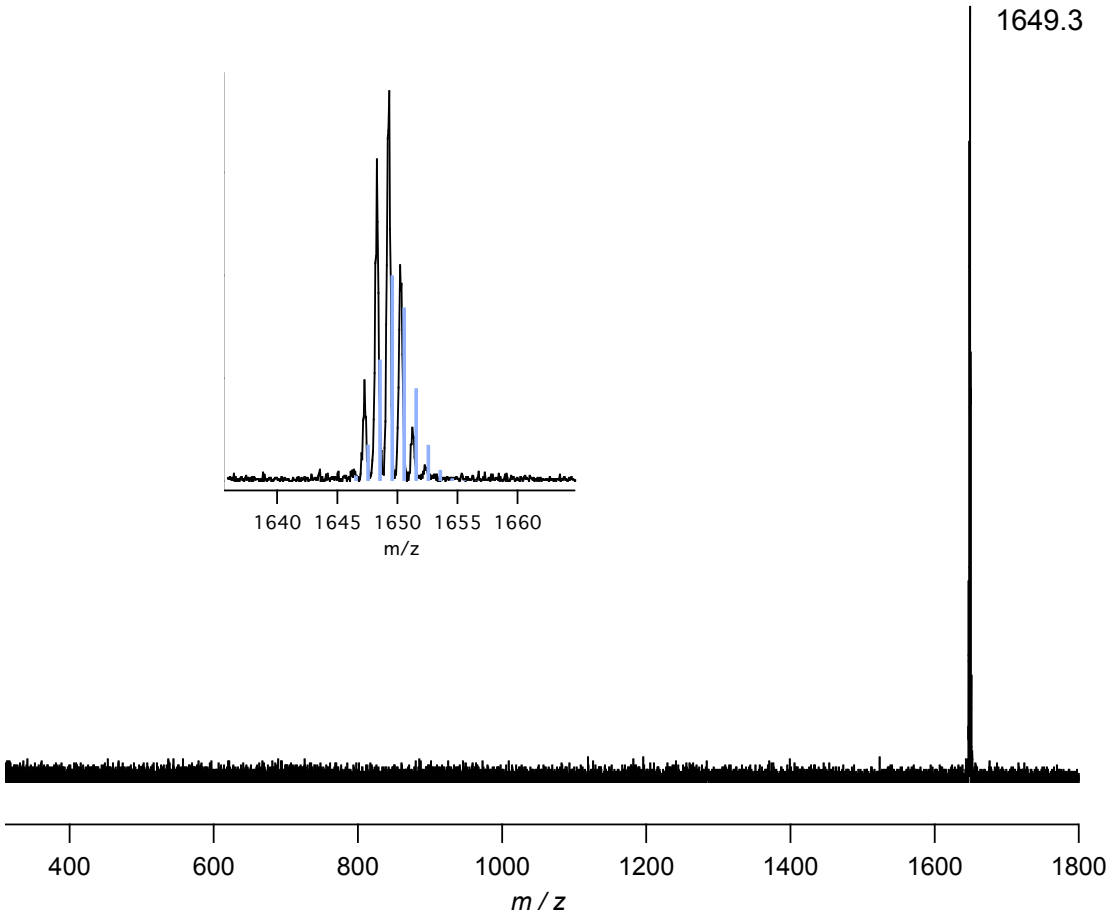

Fig. S2 MALDI-TOF mass spectrum of **4**. Insert shows the magnified spectrum (black line) and the calculated isotope pattern (blue bar).

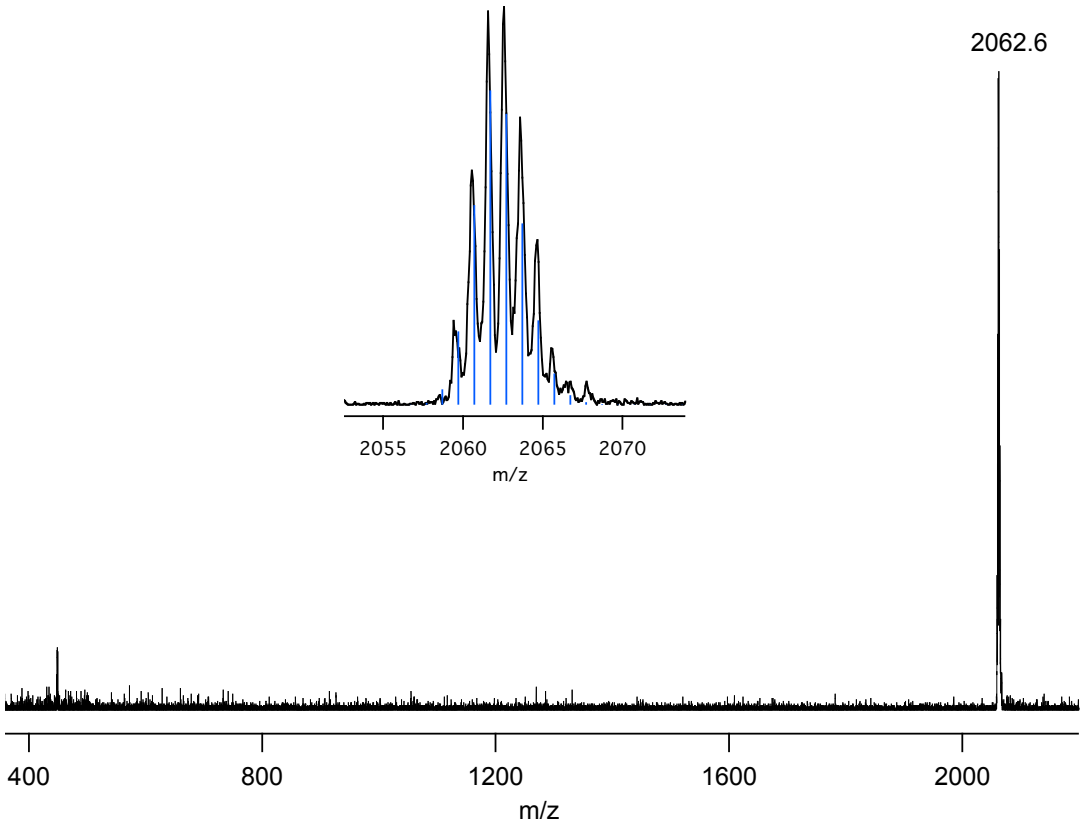

Fig. S3 MALDI-TOF mass spectrum of **5**. Insert shows the magnified spectrum (black line) and the calculated isotope pattern (blue bar).

5. UV/Vis spectra of 3, 4 and 5

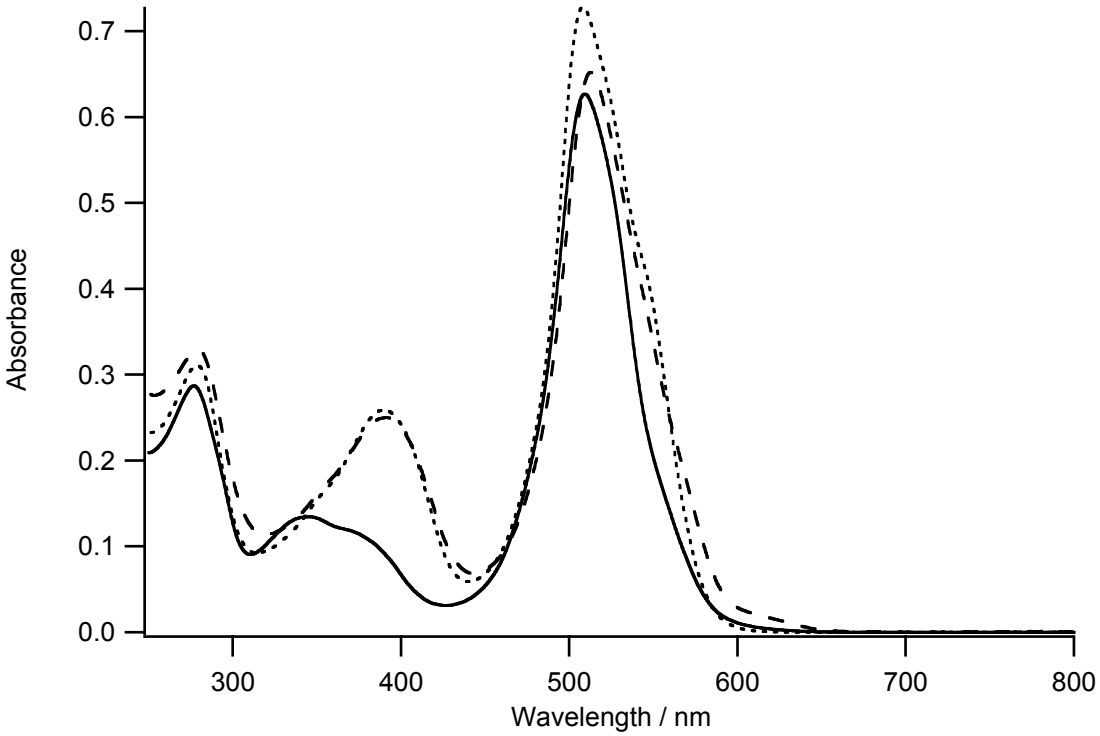

Fig. S4 UV-Vis absorption spectra of **3**(—), **4**(---), and **5**(– –) recorded in $CHCl_3$.

6. ^{1}H NMR spectra of 3 in the presence of guest cations

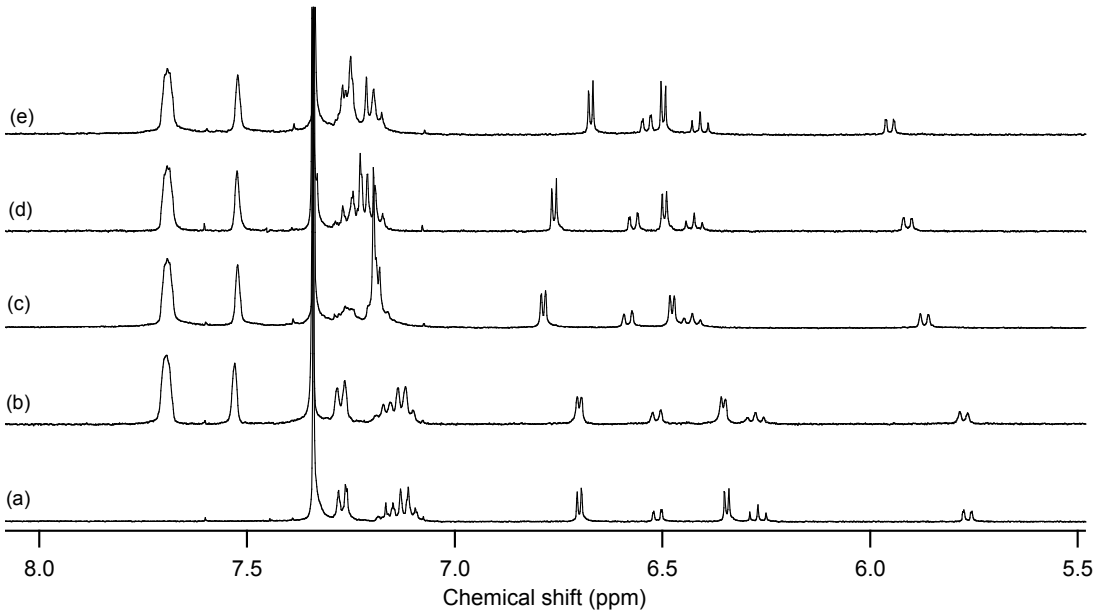

Fig. S5 ^{1}H NMR spectra of (a) **3** (0.5 mM) in $CDCl_3/CD_3OD$ (9/1) in the presence of 2.0 equiv of (b) NaTFPB, (c)KTFPB, (d)RbTFPB, and (e)CsTFPB.

7. Proposed structures of 3 with guest cations[1]

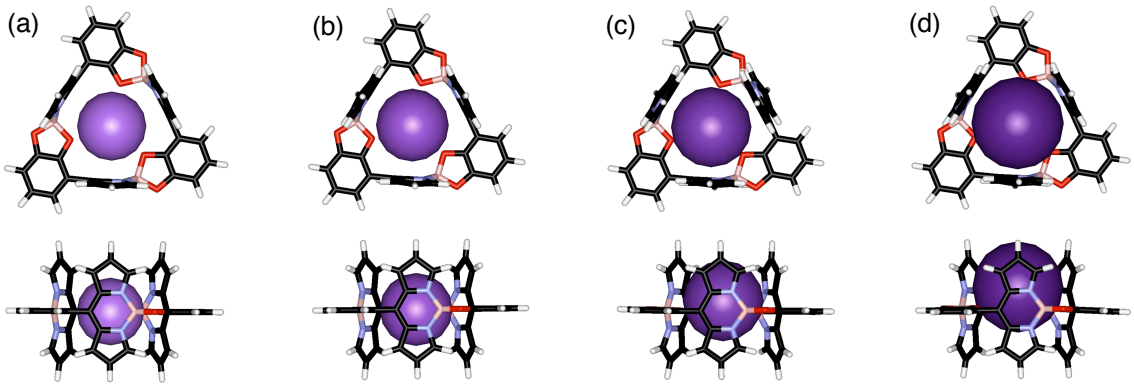

Fig. S6 Proposed cation-binding structure of **3** generated by Hartree-Fock calculations at the 3-21(*) level. Calculation with (a) Na^+, (b) K^+, (c) Rb^+, and (d) Cs^+, were carried out without phenyl groups to reduce the machine time. Color: C black, H white, B pink, N blue, O red, and the alkali metal cations are shown in purple. Distances between cation centers to oxygen atoms are (a) 2.75 Å, (b) 2.79 Å, (c) 2.88 Å, and (d) 3.15 Å and the shortest distances between cation centers to pyrrole-α carbon is (c) 3.56 Å and (d) 3.61 Å.

Reference

1 *Spartan04* for Windows; Wavefunction, Inc.: Irvine, CA.

2 The relative error in *K* is realistically minimized by working in the range of "molar fraction of the host-guest complex" ≈ 0.2 to 0.8. see "K. A. Connors, in *Binding Constants,* Wiley, 1987, ch. 2, pp. 65-69.