Cation recognition and pseudorotaxane formation of tris-dipyrrin BF_2 macrocycles†

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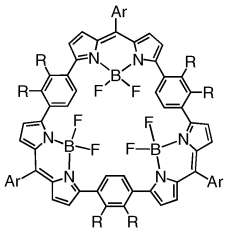
Received 3rd June 2010, Accepted 29th July 2010
DOI: 10.1039/c0cc01717e

Macrocyclic planar tris-dipyrrin BF_2 complexes exhibit strong alkali-metal recognition and pseudorotaxane formation ability with a secondary ammonium salt through BF_2–cation interactions.

Fluorinated organic compounds exhibit unique non-covalent interactions[1] such as CF···H-X (X: C, N, O),[2] CF···FC,[3] CF···M^+,[4] and perfluorobenzene···benzene,[5] which are very important in medicinal[1a] and separation chemistry[6] as well. Although fluorine-assisted interactions of a B–F moiety in neutral organic compounds would be effective due to significant difference in electronegativity between boron and fluorine atoms, such interactions have not been employed for molecular recognition. Our DFT calculation suggests that the BF_2 moiety is electronically delocalized along the B–F bond to make the fluorine partially negative[7] due to the large electronegativity difference and small atomic radius of the fluorine (see ESI†). Thus, the fluorine atom should interact with metal cations or cationic molecules. We conceived that 4,4-difluoro-4-bora-3a,4a-diaza-*s*-indecene (BODIPY)[8] is an ideal candidate for a host building block to provide efficient B–F···M^+ interactions because (1) the BF_2 moiety can work as either a monodentate or bidentate chelating recognition site, (2) the interaction can be followed by the change in the optical properties, and (3) the BODIPY framework can be easily modified to allow the interaction with the BF_2 site to be fine tuned. Neverthless, the BF_2 moiety of BODIPY has not been used for supramolecular complexation.

Herein we designed macrocyclic planar tris-dipyrrin BF_2 complexes **1** and **2** because (1) the macrocyclic framework should possess a well preorganized binding site with the six fluorine atoms facing inward, (2) rotation of the *p*-phenylene moieties should afford suitable flexibility required for guest recognition, and (3) guest recognition in the cavity may affect the optical properties of the macrocycle. Additionally, we report cation recognition by the dipyrrin BF_2 complexes and pseudorotaxane formation with a secondary ammonium salt through the BF_2···H hydrogen bonds in a bifurcated manner.

Treatment of the corresponding dipyrrin macrocycle[9] with $BF_3{\cdot}OEt_2$ in the presence of ethyl diisopropyl amine gave tris-dipyrrin BF_2 complexes **1** and **2** in 29% and 99% yields, respectively. X-ray crystallographic analysis revealed **2** has a



1 : R = H, Ar = mesityl
2 : R = OMe, Ar = Ph

planar triangular structure with a 4 Å cavity.[10]‡ The electrostatic potential surfaces (EPSs) based on the structure indicated the fluorine atoms are negatively charged (Fig. 1). The X-ray structure of **2** showed that the phenylene rings are tilted with an average dihedral angle of 52°. The DFT calculations showed the structure with the less tilted phenylene rings in **1** (32°)[11] compared to **2** (55°) because the methoxy groups in **2** face outward to decrease the steric repulsion (see ESI†). The CPK model also supported the finding that the OMe moieties in **2** are not oriented inward. However, the methoxy protons in the ^{1}H NMR spectrum of **2** appeared as a sharp singlet at 3.80 ppm, indicating that the phenylene rings flip fast on the ^{1}H NMR time scale.

UV-vis spectroscopy confirmed strong interactions of **1** and **2** with cationic guests. We employed a superweak and hydrophobic base, tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (TFPB), as an counter anion of the guests because these salts are soluble in usual organic solvents. The addition of caesium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (CsTFPB) to **1** and **2** in $CHCl_3$–CH_3OH (10 : 1) decreased the absorption at 552 and 531 nm with a concomitant increase in the absorption at 540 and 522 nm (Fig. 2). UV-vis titration suggested the formation of a 1 : 1 complex. The log K_a (M^{-1}) value for Cs^+ was determined to be 4.9 ± 0.1 by a nonlinear-least-squares regression. **1** and **2** showed size-selective binding, and the largest K_a values were observed in Cs^+ (Table 1) probably because the cavity sizes (*ca.* 4 Å) of **1** and **2** are close to the

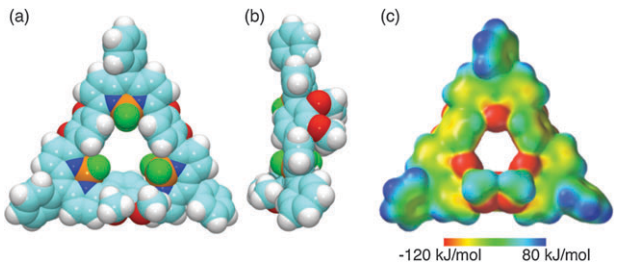


Fig. 1 (a), (b) Molecular structure of **2**. Solvent molecules are omitted for clarity. Color: C, sky-blue; H, white; B, orange; F, green; N, blue; O, red. (c) Electrostatic potential surfaces (EPSs) of **2** generated at the B3LYP/6-31G* level.

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† Electronic supplementary information (ESI) available: Experimental details and crystallographic data. CCDC 680144 and 767041. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0cc01717e

Cs^+ ionic diameter (3.34 Å).[12] **2** had a higher Cs^+ affinity than **1** (Table 1). The stronger binding of **2** may be ascribed to the larger tilting angle compared to the phenylene rings of **1**. Interaction of the counter anion TFPB with the hosts were negligibly small because *n*-Bu_4N·TFPB caused no change in the absorption spectra of the hosts due to superweak basicity of TFPB.

^1H, ^{11}B, and ^{19}F NMR spectra confirmed the formation of the metal complexes. The ^1H NMR spectra of **1**·Cs^+ and **2**·Cs^+ in $CDCl_3$–CD_3OD (10 : 1) showed significant upfield shifts ($\Delta\delta$ = −0.24 and −0.27 ppm, respectively) of the *p*-phenylene ring proton resonances compared to those of **1** and **2**.[13] Notably, the change in the methoxy proton resonance of **2** was negligible upon the addition of Cs^+, indicating that the methoxy oxygen atoms of **2** do not contribute to cation binding. The ^{19}F NMR spectra of **1** showed a characteristic downfield shift ($\Delta\delta$ = 2.1 ppm),[14] which is ascribed to the BF···Cs^+ interaction. The ^{11}B signal shifted slightly upfield upon Cs^+ complexation ($\Delta\delta$ = −0.4 ppm).

3 **4**

Next we examined the interactions of **1** and **2** with di-*n*-butylammonium (**3**) and dibenzylammonium hexafluorophosphates (**4**). The 1 : 1 complex formation was ascertained by ^1H NMR titration in $CDCl_3$ and Job plots. The ^1H NMR spectra of the mixtures with different mole ratios of **2** and **3** showed the time-averaged signals at room temperature. However, at 218 K, complexation and decomplexation were sufficiently slow on the ^1H NMR time scale because a 1 : 2 mixture of **2** and **3** gave two independent sets of signals for the **2**·**3** complex and free **3**. Furthermore, NOE correlations were observed at 218 K between the N^+–CH_2 protons of **3** and the phenylene protons of **2**. The MALDI-TOF mass spectra showed a strong peak at *m*/*z* 1336.5, which is assigned to the **2**·**3** ion. Additionally, complexation of **2** with **3** was monitored by the UV-vis spectral changes with a hypsochromic shift (11 nm). Spectroscopic titration indicated **1** and **2** have strong affinities to **3**. In addition, **2** showed an emission increase upon binding to **3** in a significant on-off fashion (**2**: λ_{max} 670 nm, Φ < 1%, **2**·**3**: 700 nm, 10%). In sharp contrast, **2** did not

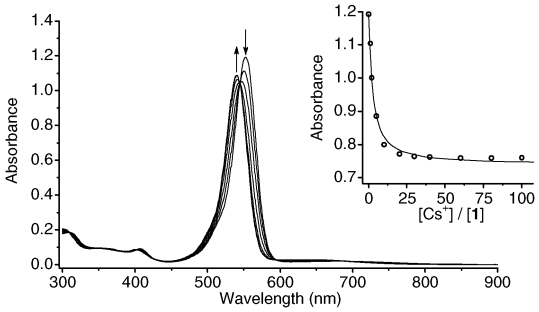

Fig. 2 UV-vis spectral changes of **1** upon the addition of CsTFPB. Inset shows the binding isotherm recorded at 552 nm with the calculated 1 : 1 binding curve (solid line): [**1**] = 4.0 μM, 0 ≤ [Cs^+]/[**1**] ≤ 100, $CHCl_3$–CH_3OH (10 : 1).

Table 1 log K_a values of **1** and **2**

	Na^+	K^+	Rb^+	Cs^+	**3**
1	2.3 ± 0.1	3.6 ± 0.1	4.04 ± 0.07	4.9 ± 0.1	3.1 ± 0.2
2	1.9 ± 0.1	4.06 ± 0.03	4.6 ± 0.1	5.5 ± 0.1	4.1 ± 0.1

K_a (in M^{-1}) determined from the UV-vis spectral changes in $CHCl_3$–CH_3OH (10 : 1), assuming a 1 : 1 stoichiometry.

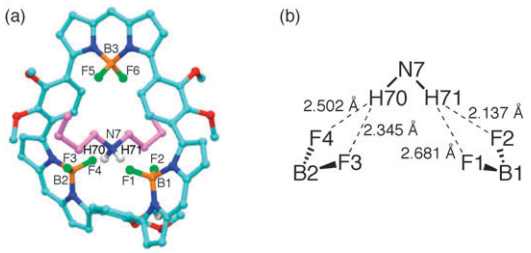

Fig. 3 (a) Ball-and-stick (side view) and (b) partial structure of the binding site of pseudo[2]rotaxane **2**·**3**. Phenyl groups and most of hydrogen atoms in (a), counter anion, and solvent molecule are omitted for clarity. Color: C, sky-blue (for **2**) and pink (for **3**); H, white; B, orange; F, green; N, blue; O, red.

interact with **4** because spectral changes were not observed. This observation well rationalizes the proposed pseudorotaxane-type binding mode by the cavity because the phenyl ring of **4** (*ca.* 7 Å) is even larger than the cavity diameters of **1** and **2**. All these results are consistent with pseudorotaxane formation of **1** and **2** with **3** in solution.

X-ray crystallographic analysis clarified the pseudorotaxane structure of **2**·**3** (Fig. 3).‡ The ammonium ion **3** was threaded through the cavity of **2** as seen in reported pseudorotaxane.[15] The ammonium nitrogen N(7) was located near B(1) and B(2). The estimated distances between the NH proton, H(71) or H(70), and the fluorine atoms F(1), F(2), or F(3), F(4) were significantly less than 2.9 Å (Fig. 3b).[1b] Therefore, the pseudorotaxane structure is maintained by the non-classical chelating hydrogen bonds, that is, bifurcated BF_2···H–N interactions.

In conclusion, neutral macrocycles **1**, **2**, which contain the BF_2 moieties, strongly bind alkali metal ions as well as organic cationic guest **3** through novel BF_2–cation interactions. This new interaction should be applicable in a variety of molecular recognition systems, including rotaxanes with a highly functional "*rota*" moiety based on the conjugated macrocycle with intriguing optical properties.

We thank Prof. T. Akasaka, Univ. of Tsukuba, for the MALDI-TOF mass measurements. This research was financially supported by Grants-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

Notes and references

‡ *Crystallographic data* for **2**·3$CHCl_3$: $C_{72}H_{54}B_3Cl_9F_6N_6O_6$, M_r = 1564.69, monoclinic, space group $P2_1/n$ (no. 14), a = 16.94(3) Å, b = 20.22(4) Å, c = 20.85(5) Å, β = 95.87(8)°, V = 7103(26) Å^3, Z = 4, ρ_c = 1.463 gcm^{-3}, μ = 0.428 mm^{-1}, $Mo_{K\alpha}$ radiation (λ = 0.71075 Å), T = 120(2) K, $2\theta_{max}$ = 50°, 52 087 reflections measured, 12 381 unique (R_{int} = 0.1355), R_1 = 0.0845 ($I > 2\sigma(I)$), wR_2 = 0.2251 (all data), GOF (F^2) = 1.002, $\Delta\rho_{max}/\Delta\rho_{min}$ = 0.515/−0.446 eÅ^{-3}. The structure was solved by direct methods. CCDC

680144 contains 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.[16]

Crystallographic data for **2**·**3**·PF_6·C_7H_8: $C_{84}H_{79}B_3F_{12}N_7O_6P_2$, M_r = 1573.94, monoclinic, space group $P2_1$ (no. 4), a = 12.38(13) Å, b = 15.96(15) Å, c = 19.32(17) Å, β = 102.48(3)°, V = 3727(6) Å^3, Z = 2, ρ_c = 1.402 gcm^{-3}, μ = 0.129 mm^{-1}, $Mo_{K\alpha}$ radiation (λ = 0.71075 Å), T = 120(2) K, $2\theta_{max}$ = 50°, 29 402 reflections measured, 13 051 unique (R_{int} = 0.1331), R_1 = 0.0909 ($I > 2\sigma(I)$), wR_2 = 0.2641 (all data), GOF (F^2) = 1.030, $\Delta\rho_{max}/\Delta\rho_{min}$ = 0.458/–0.514 eÅ^{-3}. The structure was solved by direct methods. CCDC 767041 contains 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.[16]

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10 A centroid of the six fluorine atoms was estimated by X-ray crystallographic data. The average distance between the centroid and fluorine atoms was calculated to be *ca.* 3.6 Å. The van der Waals radius of fluorine atom is 1.47 Å.[17] Thus, the diameter of cavity is *ca.* 4 Å.

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