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Nestable Tetrakis(spiroborate) Nanocycles

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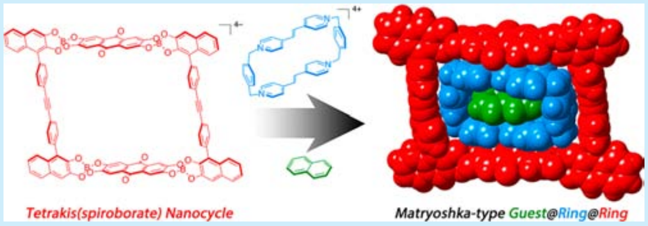
S *Supporting Information*

ABSTRACT: Multicomponent construction of the tetrakis(spiroborate) anionic nanocycles was achieved by reacting bis(dihydroxynaphthalene)s with tetrahydroxyanthraquinone in the presence of boric acid in a self-organized manner. These nanocycles exhibited selective molecular recognition behavior toward cationic guests such as methyl viologen derivatives. Formation of a supramolecular ring@ring and a guest@ring@ring structure was observed by combining the anionic nanocycle and the vinylogous analog of cyclobis(paraquat-*p*-phenylene).



Shape-persistent macrocycles have been designed and prepared for various purposes, including their use as hosts for molecular recognition and the construction of porous stacking structures.[1] Particularly for molecular recognition, their shape persistence plays an important role in the strict shape- and size-selective guest inclusion. The cyclic structures are usually constructed with a combination of rigid components, such as aromatic rings and ethynylene linkages. Stoddart and co-workers have continuously demonstrated that cyclobis(paraquat-*p*-phenylene) (blue box) and its derivatives act as good host molecules for the recognition of various electron-rich aromatic compounds.[2] In addition to the finely adjusted cavity size, their tetracationic nature allows them to have strong affinity toward electron-rich aromatic guests. To the best of our knowledge, however, there are only a few examples of anionic shape-persistent macrocycles that selectively recognize electron-deficient or cationic aromatic guests.[3] The combination of cationic and anionic macrocycles is expected to afford new supramolecular higher-order architectures.

Previously, we have reported that *rac*-2,2′,3,3′-tetrahydroxy-1,1′-binaphthyl reacts with an equimolar amount of boric acid in *N*,*N*′-dimethylformamide (DMF) to afford a cyclic trimeric structure in a self-organized manner via the formation of spiroborate linkages.[4] The tris(spiroborate) cyclophane is trianionic and sufficiently shape-persistent to form a rigid triangular structure. As the next step, we intend to apply our spiroborate strategy to the multicomponent construction of supramolecular structures. Herein we present the preparation of the shape-persistent spiroborate nanocycles by the use of two different bis(dihydroxyarene) derivatives and boric acid. We also demonstrate the construction of a Matryoshka-type, nestable guest@ring@ring associate via the multilayered molecular recognition of the spiroborate nanocycle and the blue box derivatives.

Spiroborate anionic nanocycles were prepared by mixing 1,4-bis(1-(2,3-dihydroxynaphthyl))benzene (**1a**′), previously generated by deprotection of 1,4-bis(1-(2-methoxymethoxy-3-hydroxynaphthyl))benzene (**1a**), and 2,3,6,7-tetrahydroxyanthraquinone (**3**) in the presence of 2 equiv of boric acid in DMF at 150 °C (Scheme 1). The reversible formation of a spiroborate linkage occurred, and tetrakis(spiroborate) nanocycle $\mathbf{4a}\cdot(\mathrm{Me_2NH_2})_4$ was quantitatively obtained after reprecipitation with diethyl ether. The preparation of the spiroborate nanocycle $\mathbf{5a}\cdot(\mathrm{Me_2NH_2})_4$, which has a larger ring size, was also achieved by the use of bis(4-(1-(2,3-dihydroxynaphthyl))phenyl)acetylene (**2a**′) instead of **1a**′. In addition, the tetrabutylated derivative of each nanocycle ($\mathbf{4b}\cdot(\mathrm{Me_2NH_2})_4$ and $\mathbf{5b}\cdot(\mathrm{Me_2NH_2})_4$) was prepared in a similar manner.

We have reported that cyclic spiroborate trimer *rac*-$\mathbf{6}\cdot(\mathrm{Me_2NH_2})_3$ was formed when **1a**′ was treated with an equimolar amount of boric acid in DMF (Scheme 2).[4b] This system involved only **1a**′ as a sole bis(dihydroxyarene) component and gave thermodynamically stable cyclic trimer $\mathbf{6}^{3-}$ as the main product in low isolated yield (~20%). By ^{1}H NMR monitoring, **1a**′ was converted into $\mathbf{6}^{3-}$ after stirring with boric acid in DMF at 150 °C for 24 h, although some byproducts were also formed (Figure 1). In contrast, sufficient conversion into nanocycle $\mathbf{4a}^{4-}$ took place by the addition of an equimolar amount (based on **1a**′) of **3** and additional boric acid, and $\mathbf{6}^{3-}$ almost completely disappeared, indicating that the construction of nanocycle $\mathbf{4a}^{4-}$ was more favorable than the formation of cyclic trimer $\mathbf{6}^{3-}$. Rotational freedom of three **1a**′ would prevent the sufficient convergence into $\mathbf{6}^{3-}$, whereas the intervention of **3** diminished the structural flexibility of the

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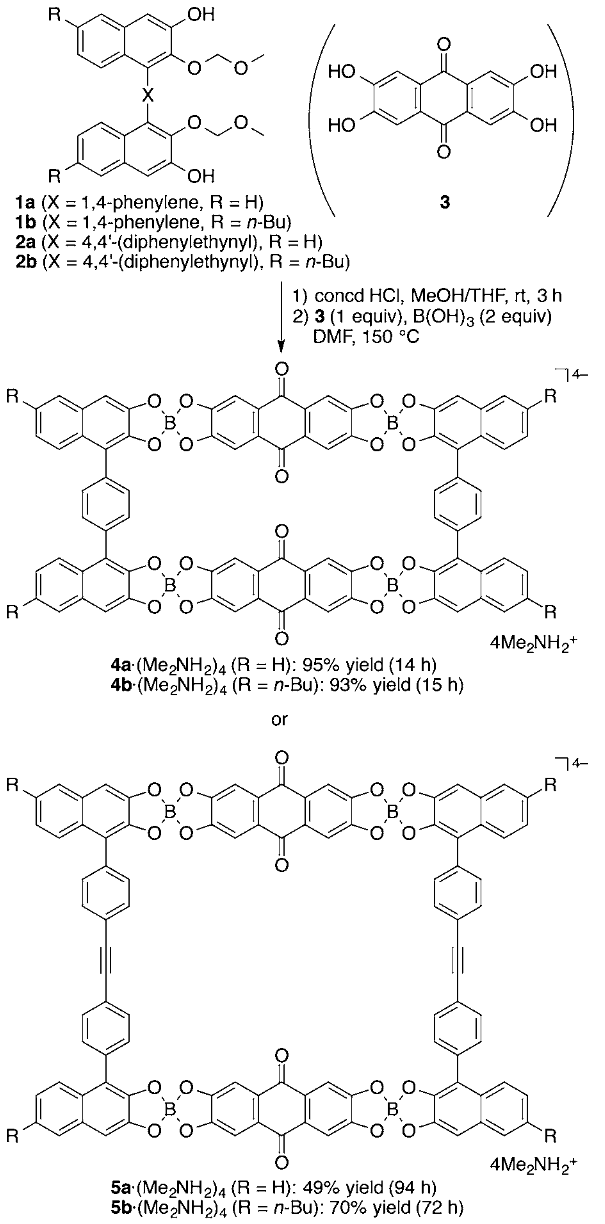
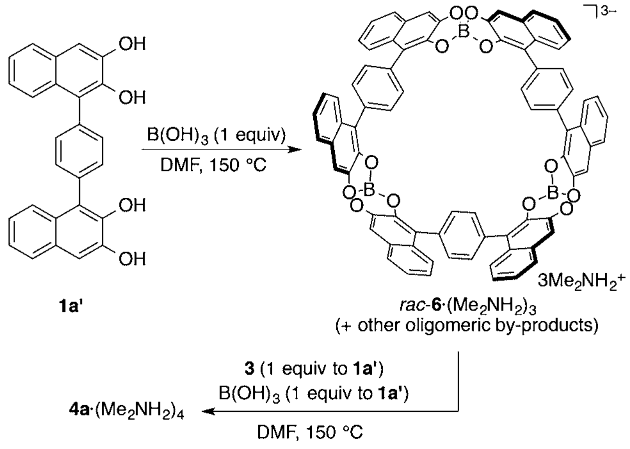
Scheme 1



Scheme 2



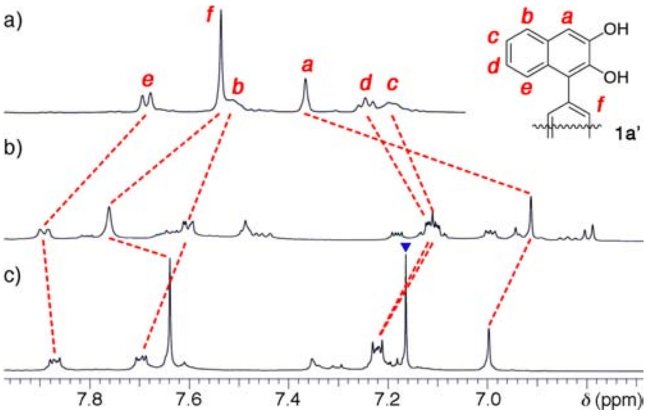


Figure 1. Partial ^{1}H NMR spectra (500 MHz, 25 °C in DMF-d_7) of (a) **1a**′ (40 mM); (b) **1a**′ (40 mM) and $B(OH)_3$ (40 mM) after heating at 150 °C for 24 h; and (c) adding **3** (40 mM), and $B(OH)_3$ (40 mM) to (b), and then heating at 150 °C for an additional 3 h. A signal marked by a blue triangle was assigned to the proton derived from **3**.

intermediates and led to the efficient formation of **4a**$^{4-}$. The multicomponent construction of various spiroborate higher-ordered structures can be realized by the rational design of bis(dihydroxyarene) components.

The precise structure of spiroborate nanocycle **4a**$^{4-}$ was determined by single crystal X-ray diffraction analysis in the form of its tetra(*n*-butyl)ammonium (TBA) salt (Figure 2).[5] It was confirmed that **1a**′ and **3** were alternatively bound through a spiroborate linkage to form a rectangular macrocycle bearing a thin box-shaped cavity. The distance between the centers of the two anthraquinone units was estimated to be 7.7 Å, whereas the distance between the two centroids of the upper and lower naphthalene rings was found to be 8.7 Å. The cavity size of **4a**$^{4-}$ would be varied over a certain range and able to fit aromatic guests.

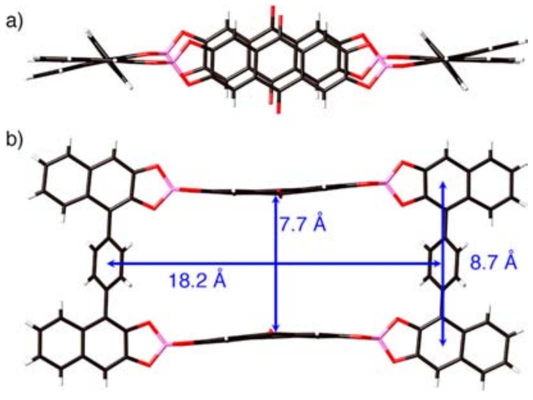


Figure 2. Crystal structure of spiroborate nanocycle **4a**·$(TBA)_4$. Top (a) and front (b) views. Counterions (TBA^+) and solvent molecules (DMF) are omitted for clarity.

The guest inclusion behavior of spiroborate nanocycle **4b**$^{4-}$ was evaluated by the use of 1,2-bis(4-pyridyl)ethylene (**7**) and 1,2-bis(4-(1-methylpyridinium))ethylene dication (**8**$^{2+}$) as electrically neutral and cationic guests, respectively (Figure 3). In ^{1}H NMR measurement, almost no interaction was observed between **4b**$^{4-}$ and **7**, whereas a significant upfield shift and signal broadening were found upon mixing **8**$^{2+}$ and **4b**$^{4-}$ in DMSO-d_6, indicating selective molecular recognition of the

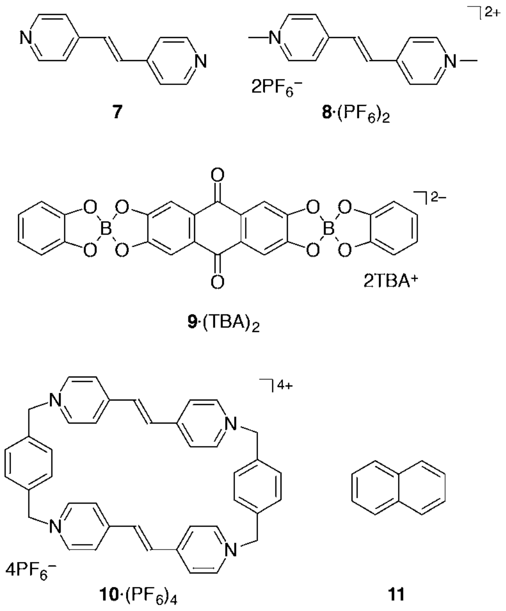


Figure 3. Chemical structure of **7**, **8**·$(PF_6)_2$, **9**·$(TBA)_2$, **10**·$(PF_6)_4$, and **11**.

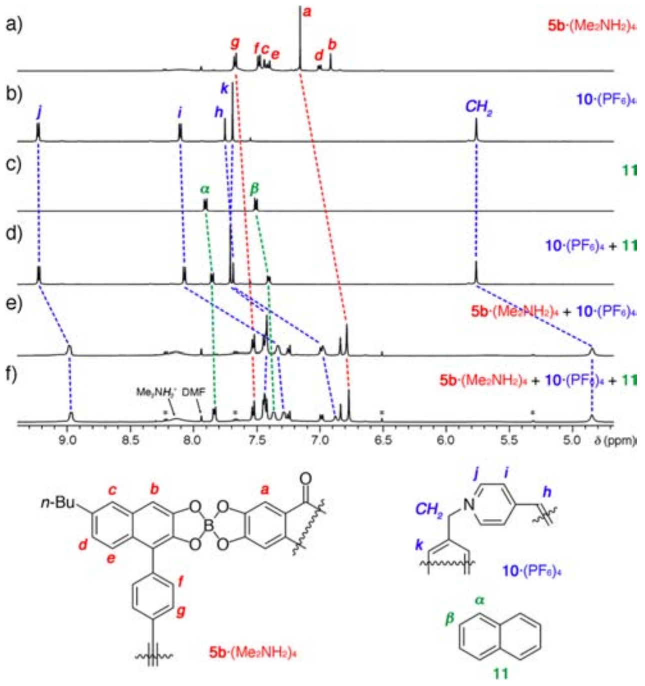


Figure 4. Partial ^1H NMR spectra (500 MHz, 25 °C in DMSO-d_6) of (a) **5b**·$(Me_2NH_2)_4$ (0.5 mM); (b) **10**·$(PF_6)_4$ (0.5 mM); (c) **11** (0.5 mM); (d) **10**·$(PF_6)_4$ (0.5 mM) and **11** (0.5 mM); (e) **5b**·$(Me_2NH_2)_4$ (0.5 mM) and **10**·$(PF_6)_4$ (0.5 mM); and (f) **5b**·$(Me_2NH_2)_4$ (0.5 mM), **10**·$(PF_6)_4$ (0.5 mM), and **11** (0.5 mM). Signals marked by an asterisk (*) are assigned to impurities.

cationic guest (Figure S1). The upfield shift of the anthraquinone proton signals and the downfield shift of the phenylene proton signals were also observed for **4b**$^{4-}$, implying that nanocycle **4b**$^{4-}$ recognized **8**$^{2+}$ inside the cavity. This is also supported by the fact that a only small upfield shift and broadening was observed when **8**·$(PF_6)_2$ was treated with acyclic bis(spiroborate) **9**·$(TBA)_2$, probably indicating the existence of electrostatic and weak $\pi-\pi$ interactions (Figure S2). The cyclic structure would be essential for sufficient host−guest interaction. According to the Job plot, the association ratio of **4b**$^{4-}$ and **8**$^{2+}$ was estimated to be 1:2 (Figure S3). The width of the cavity of **4b**$^{4-}$ was estimated to be ca. 18 Å and enough to incorporate two **8**$^{2+}$. The electrostatic balancing also might cause this stoichiometry.

Spiroborate nanocycle **5**$^{4-}$ possessed a larger ring size and was expected to exhibit different molecular recognition behavior from **4**$^{4-}$. The distance between the two anthraquinone units of spiroborate nanocycle **5**$^{4-}$ was estimated to be ca. 14−16 Å by a provisional molecular modeling study, which would be suitable for the incorporation of three aromatic planes. According to this estimation, we tried to employ the vinylogous analog of the blue box (**10**$^{4+}$)[2c] as a guest, which was proven to well recognize aromatic compounds in its electron-deficient cavity to form three-layered tetracationic aromatic stacks (Figure 3).[6] By ^1H NMR measurement, it was confirmed that the proton signals of both **10**$^{4+}$ and naphthalene (**11**) were shifted when the two compounds were mixed in DMSO-d_6, indicating that their association took place (Figure 4d). The precise structure of the associate was determined by single crystal X-ray diffraction analysis, showing that **11** was incorporated inside the cavity of **10**$^{4+}$ (Figure S5). It was also found that **10**$^{4+}$ acted as a guest for the tetraanionic spiroborate nanocycle. In the presence of **5b**$^{4-}$, All the proton signals of **10**$^{4+}$, including the methylene protons located outside its cavity, were shifted upfield while keeping the symmetricity of the spectrum (Figure 4e). A further upfield shift (*h* and *i*) and slight downfield shift (*k*) of the proton signals of **10**$^{4+}$, similar to those in Figure 4d, were observed when **11** was added to the mixture of **5b**$^{4-}$ and **10**$^{4+}$ (Figure 4f). In addition, the upfield shift of the methylene proton signals of **10**$^{4+}$ was preserved after the addition of **11**. These data implied that **10**$^{4+}$ was incorporated into the cavity of **5b**$^{4-}$ while keeping its association with **11**. This was confirmed by an NOESY experiment, in which multiple correlations were observed between **5b**$^{4-}$ and **10**$^{4+}$, and **10**$^{4+}$ and **11** in their 1:1:1 mixture (Figure S6). The cold spray ionization mass spectrometry (CSI-MS) experiment also supported their multicomponent association behavior.[7] When a mixture of **5b**·$(Me_2NH_2)_4$, **10**·$(PF_6)_4$, and **11** in DMF/MeOH was sprayed in the positive-ion mode at rt, a series of signals corresponding to the 1:1:1 complex of **5b**$^{4-}$, **10**$^{4+}$, and **11** were detected (Figure S7).

The complexation mode of **5a**$^{4-}$, **10**$^{4+}$, and **11** was unambiguously determined by X-ray crystallographic analysis (Figure 5). The Matryoshka-type, nestable guest@ring@ring

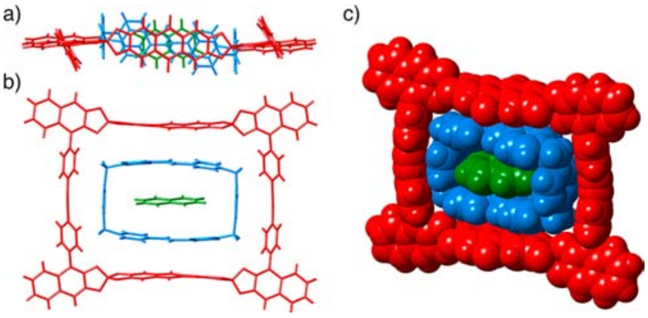


Figure 5. Crystal structure of **11@10@5a**. Top (a) and front (b) views shown by stick model, and (c) bird's eye view shown by a space filling model. **5a**$^{4-}$, **10**$^{4+}$, and **11** are drawn in red, blue, and green, respectively. Solvent molecules (DMF) and excess **11** are omitted for clarity.

structure was constructed to afford a pentalayered aromatic stack.[8] All the longitudinal axes of the two anthraquinone moieties of **5a**$^{4-}$, the two vinylenebispyridinium moieties of **10**$^{4+}$, and **11** were almost parallel, and the distance of each pair of the adjacent aromatic planes was ca. 3.5 Å, which would be suitable for aromatic $\pi-\pi$ interaction. In addition, the $\pi-\pi$ and methylene CH−π interactions between the diphenylethynyl linkage of **5a**$^{4-}$ and the *p*-xylylene linkage of **10**$^{4+}$, and the aromatic CH−π interactions between the *p*-xylylene linkage of **10**$^{4+}$ and **11**, were also found. Those interactions would be important for the parallel association of **11@10@5a**.

In summary, we have reported the preparation of shape-persistent tetraanionic spiroborate nanocycles **4**$^{4-}$ and **5**$^{4-}$ by reacting bis(dihydroxynaphthalene) (**1**,**2**) with tetrahydroxy-anthraquinone **3** in the presence of boric acid in a self-organized manner. Spiroborate nanocycle **4b**$^{4-}$ exhibited molecular recognition ability toward cationic aromatic guest **8**$^{2+}$, whereas no interaction was observed between **4b**$^{4-}$ and electrically neutral guest **7**. Spiroborate nanocycle **5**$^{4-}$, bearing a larger ring size, also showed inclusion behavior toward its cationic guest. The vinylogous analog of cyclobis(paraquat-*p*-phenylene) **10**$^{4+}$ was incorporated into **5**$^{4-}$ to form **10@5**, a supramolecular ring@ring structure. Furthermore, a three-component association was realized by mixing **5**$^{4-}$, **10**$^{4+}$, and naphthalene (**11**) to form **11@10@5** as a Matryoshka-type, nestable guest@ring@ring supramolecular structure. The formation of these associates was observed in solution and the solid state by NMR, CSI-MS, and X-ray crystallographic analyses.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Detailed experimental procedures for synthesis and characterization of all new compounds, NOESY NMR and CSI-MS data of **11@10@5a**, and X-ray diffraction data of **9**·$(\mathrm{TBA})_2$, [**11@10**]·$(\mathrm{PF}_6)_4$, **10@5b**, and **11@10@5a** in the form of single-crystal X-ray crystallographic information files (CIF). This materials is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(5) CCDC-1045666 (**10@5b**), 1045667 ([**11@10**]·$(\mathrm{PF}_6)_4$), 1045668 (**11@10@5**), 1045669 (**4a**·$(\mathrm{TBA})_4$), and 1045670 (**9**·$(\mathrm{TBA})_2$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk.

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