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# Back to Back Twin Bowls of $D_3$-Symmetric Tris(spiroborate)s for Supramolecular Chain Structures

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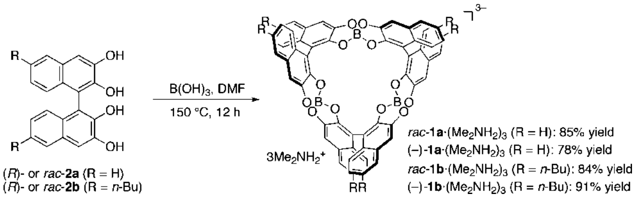
Increasing attention has been paid to the development of supramolecular polymers for the creation of functionalized nanomaterials.[1−3] Recent studies have shown that host−guest compounds, such as cyclodextrins,[4] calixarenes,[5] cyclophanes,[6] donor−acceptor molecules,[7] and crown ethers,[8] could be effectively employed as a component of polymer architecture and that strong intermolecular force between monomer units could be achieved by rationally designing host and guest moieties. In all of those studies, the basic strategy involved covalent bond formation between two molecular recognition moieties (host−host, guest−guest, or host−guest) through appropriate tethers to achieve iterative intermolecular interaction. Although this strategy allows us to employ various types of monomer units, relatively complicated chemical functionalization of both host and guest moieties is sometimes required. In this manuscript, we present the design and preparation of a new class of back to back twin bowls of $D_3$-symmetric tris(spiroborate) cyclophanes $\mathbf{1}^{3-}$ that exhibit molecular recognition behavior via π- and electrostatic interactions at both sides of a symmetry plane (Scheme 1).[9] Mimicking vertebrate spine, this molecular coupling behavior makes it possible to glue various cationic guest molecules to each other via dual host−guest interaction (Figure 1). Particularly in the case of cationic metal complexes, iterative clathration takes place to form supramolecular metallocopolymers. The spiroborate linkage was chosen for the spontaneous cyclophane formation because its accessibility and unique thermodynamic behavior allowed us to obtain highly symmetric cyclic structures from simple bis(dihydroxyarene) unit in a self-organization manner.[10−12]

***Scheme 1.*** Preparation of Cyclophane $\mathbf{1}\cdot(Me_2NH_2)_3$



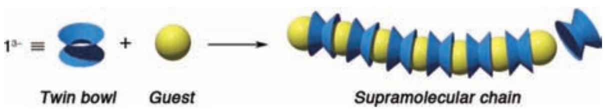


***Figure 1.*** Schematic representation of the formation of supramolecular chain structure by iterative clathration of twin-bowl-shaped cyclophane $\mathbf{1}^{3-}$ with guest molecules.

Tris(spiroborate) cyclophanes were readily prepared from 2,2′,3,3′-tetrahydroxy-1,1′-binaphthyls **2** and boric acid according to Wuest's procedure (Scheme 1).[12] Equimolar amounts of *rac*-**2a** and boric acid were mixed in DMF at 150 °C to afford trimer cyclophane *rac*-$\mathbf{1a}\cdot(Me_2NH_2)_3$ in 85% yield. Dimethylamine would be generated by hydrolysis of DMF. In this reaction, almost no signals of other oligomeric structures were detected by ESI-MS analysis. Cyclophanes (−)-$\mathbf{1a}\cdot(Me_2NH_2)_3$, *rac*-$\mathbf{1b}\cdot(Me_2NH_2)_3$, and (−)-$\mathbf{1b}\cdot(Me_2NH_2)_3$ were also prepared in the same manner.

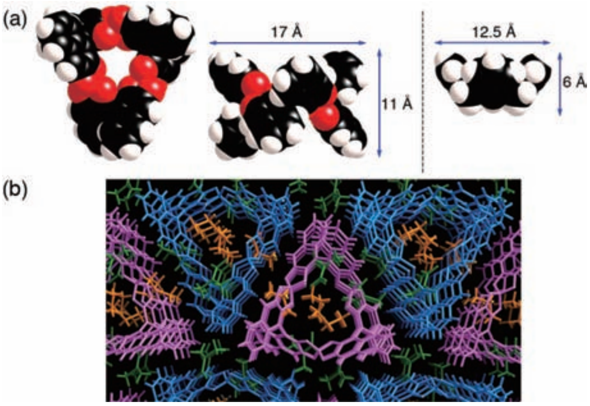


***Figure 2.*** Crystal structures of *rac*-$\mathbf{1a}\cdot(Me_2NH_2)_3$: (a) top and front views of (−)-$\mathbf{1a}^{3-}$ (left and center), and front view of calix[4]arene optimized at PM3 level calculation (right); (b) top view of columnar structures formed from (+)-$\mathbf{1a}^{3-}$ (pink), (−)-$\mathbf{1a}^{3-}$ (blue), $Me_2NH_2^+$ (orange), and DMF (green).

The structure of cyclophane *rac*-$\mathbf{1a}\cdot(Me_2NH_2)_3$ was unequivocally determined by single-crystal X-ray diffraction analysis (Figure 2).[13] All the three binaphthyl units have the same absolute configuration and are bound together through a spiroborate linkage. The estimated outer diameter and height of $\mathbf{1a}^{3-}$ are 17 and 11 Å, respectively (Figure 2a). Compared with the standard calix[4]arene (ca. 12.5 Å × 6 Å), $\mathbf{1a}^{3-}$ has wide cavities on both sides of the symmetry plane, which would be suitable for large guest molecules. Cyclophanes having the same absolute configuration are stacked to form columnar-like arrays and (+)- and (−)-columnar arrays alternatively stand side-by-side to form a stable crystal packing in which (+)- and (−)-$\mathbf{1a}^{3-}$, which are adjacent to each other, associate through complementary edge-to-face CH-π interactions between naphthalene rings with a distance of ~2.8 Å (Figure 2b). Three dimethylammonium cations are encapsulated by two cyclophanes, and this capsulelike structure is repeated almost along with the $D_3$ axis of $\mathbf{1a}^{3-}$.

To demonstrate the molecular recognition ability of $\mathbf{1}^{3-}$ in solution, we chose $[Ir(tpy)_2](PF_6)_3$ ($\mathbf{3}\cdot(PF_6)_3$) as a guest molecule (tpy: 2,2′:6′,2″-terpyridine), and the complexation of (−)-$\mathbf{1b}^{3-}$ with $\mathbf{3}^{3+}$ was monitored by $^1H$ NMR (Figure 3). The highly symmetrical structure could be observed in an acetone-$d_6$ solution of the mixture of the components. All signals of $\mathbf{3}^{3+}$ except $H_a$ were shifted upfield because of the deshielding effect of the naphthalene rings of $\mathbf{1b}^{3-}$. The downfield shift of $H_a$ signal indicates that this proton is located

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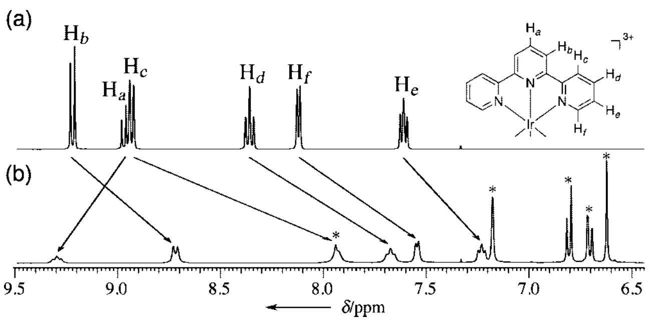

***Figure 3.*** $^1$H NMR spectra of $\mathbf{3}^{3+}$ in the absence or presence of (−)-$\mathbf{1b}\cdot(Me_2NH_2)_3$ (400 MHz, acetone-$d_6$, 25 °C): (a) $\mathbf{3}\cdot(PF_6)_3$ (6 mM); (b) (−)-$\mathbf{1b}\cdot(Me_2NH_2)_3$ (6 mM) and $\mathbf{3}\cdot(PF_6)_3$ (6 mM). Signals marked by an asterisk (*) were assigned to (−)-$\mathbf{1b}^{3-}$.

at the center of the cavity, where it would be surrounded by six oxygen atoms.

According to DOSY experiment in DMSO-$d_6$ using BPPSTE pulse sequence,[14] the diffusion constant of (−)-$\mathbf{1b}^{3-}$ was estimated to be $D = 1.5 \times 10^{-10}$ m$^2$ s$^{-1}$, which was decreased to $D = 1.2 \times 10^{-10}$ m$^2$ s$^{-1}$ by the addition of 2 equiv. of $\mathbf{3}^{3+}$, indicating that the degree of complexation of $\mathbf{1b}^{3-}$ was increased in the presence of excess amount of $\mathbf{3}^{3+}$ (see the Supporting Information, Figure S1).

The formation of the chain structure was also confirmed by cold spray ionization mass spectrometry (CSI-MS).[15] When a 1:1 mixture of (−)-$\mathbf{1b}\cdot(Me_2NH_2)_3$ and $\mathbf{3}\cdot(PF_6)_3$ in DMF/acetone was sprayed in the positive-ion mode at 25 °C, various signals derived from oligomeric structures were observed. Among them, characteristic signals could be found at $m/z$ = 2846.7, 3503.3, and 4159.2, which were assigned to $[((-)\text{-}\mathbf{1b})_4\cdot\mathbf{3}_5]^{3+}$, $[((-)\text{-}\mathbf{1b})_5\cdot\mathbf{3}_6]^{3+}$, and $[((-)\text{-}\mathbf{1b})_6\cdot\mathbf{3}_7]^{3+}$, respectively (see the Supporting Information, Figure S2).

Temperature-responsive gelation behavior was observed in this supramolecular chain system. When a solution of (−)-$\mathbf{1a}\cdot(Me_2NH_2)_3$ (10 mM) and $\mathbf{3}\cdot(PF_6)_3$ (10 mM) in *N,N,N′,N′,N″,N″*-hexamethylphosphoric triamide (HMPA) was heated above the lower critical solution temperature (LCST), phase transition rapidly occurred to produce an organogel (see the Supporting Information, Figure S3). After heating was stopped and the mixture was cooled to ambient temperature, the gel reverted to the solution phase within 15 min. This process was completely reversible, and LCST was estimated to be 78.5 °C at this concentration.

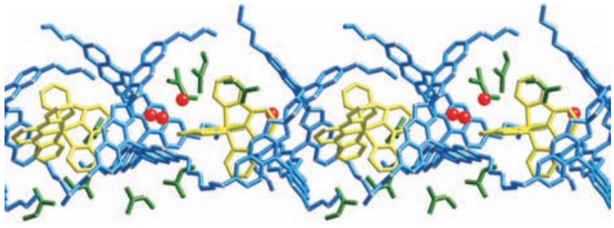

***Figure 4.*** Crystal structure of *rac*-$\mathbf{1b}\cdot\mathbf{3}$: $\mathbf{1b}^{3-}$ (blue), $\mathbf{3}^{3+}$ (yellow), water (red), and DMF (green). Hydrogen atoms are omitted for clarity.

The solid-state structure of $\mathbf{1b}\cdot\mathbf{3}$ have been elucidated by X-ray crystallographic analysis (Figure 4).[13] As expected, iterative encapsulation of $\mathbf{3}^{3+}$ by $\mathbf{1b}^{3-}$ took place to form one-dimensional array of the guest molecules. In addition, two $\mathbf{3}^{3+}$ are in van der Waals contact each other through the cavity of **1b**, showing that the spherical cationic guests were effectively glued by the cyclophane $\mathbf{1}^{3-}$.

In conclusion, we have designed and prepared a new class of bilateral cyclophanes $\mathbf{1}^{3-}$ for the construction of supramolecular chain structures by iterative host−guest interaction with ditopic guest molecules. Treatment of $\mathbf{1}^{3-}$ with Ir(III) complex $\mathbf{3}^{3+}$ in solution led to the formation of the chain structure, as confirmed by $^1$H NMR and CSI-MS studies. Especially in the case of (−)-$\mathbf{1a}^{3-}$ with $\mathbf{3}^{3+}$, the HMPA solution exhibited rapid temperature-responsive gelation behavior. Additional work and related experiments of supramolecular polymers are now under investigation.

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**Supporting Information Available:** Detailed experimental procedures for synthesis and characterization of all new compounds, DOSY and CSI-MS data, photograph of an organogel (PDF); X-ray diffraction data in the form of CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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