Halogen Bonding

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A Halogen-Bonding Catenane for Anion Recognition and Sensing**

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The field of anion supramolecular chemistry has expanded enormously during the past few decades, inspired in large part by the realization of the many fundamental roles negatively charged species play in a range of chemical, biological, medical and environmental processes.[1] Through the incorporation of complementary electrostatic, hydrogen bonding, Lewis acid–base[2] and anion–π non-covalent interactions[3] into acyclic and macrocyclic molecular framework design, numerous efficient synthetic anion receptors and sensors have been developed. However, the challenge to mimic the degree of selectivity exhibited by biological anion-binding proteins still remains. Halogen bonding (XB) is the attractive non-covalent interaction between an electron-deficient, positively polarized halogen atom, commonly bromine or iodine, and a Lewis base.[4] Anions have been exploited extensively as XB acceptors in the solid state crystal engineering[5] of conducting, magnetic and liquid-crystalline materials.[6] Given XB's complementary analogy to hydrogen bonding in terms of stringent directionality and bond strength,[7] it is surprising that solution phase applications of XB[8] in molecular recognition processes such as protein–ligand[9] complexes, anion receptor chemistry,[10] and catalysis[11] are only now beginning to emerge.

By using anion templation, we have constructed three-dimensional interpenetrated and interlocked molecular host systems that exhibit a high degree of selectivity towards the templating anion through primarily electrostatics and convergent hydrogen bonding.[12] In an effort to influence significantly the steric, electronic and lipophilic characteristics, and hence anion recognition properties, of the interlocked binding pocket, we recently reported the first XB-bonding rotaxane containing an iodotriazolium axle which selectively recognizes iodide through the combination of halogen and hydrogen bonding interactions from respectively the axle and macrocyclic components of the interlocked host system.[13] Herein we describe the anion-templated synthesis of the first XB catenane which selectively recognizes chloride and bromide anions solely by halogen bonding, through cooperative action of two bromine halogen bond donor atoms. Furthermore we demonstrate the XB catenane's ability to optically sense anions using fluorescence spectroscopy.

The target acyclic precursor bromine-functionalized imidazolium compound $\mathbf{6}^+$ was designed to incorporate complementary supramolecular interactions to facilitate the assembly of an orthogonal 2:1 host-to-guest stoichiometric complex around a halide anion template using XB (Figure 1).

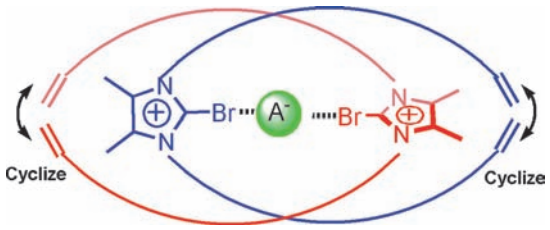

Figure 1. Schematic representation of halogen bonding anion templated assembly of an orthogonal 2:1 stoichometric complex.

The acyclic precursor molecule contains a bromine halogen bond-donating imidazolium group covalently linked through naphthalene and hydroquinone motifs to vinyl functional groups, such that highly directional, linear cooperative XB halide interactions would favor formation of the orthogonal assembly. In addition, π–π stacking interactions between the intercalated electron deficient bromoimidazolium motif and electron-rich hydroquinones are designed to further stabilize the XB-associated assembly prior to ring closing metathesis (RCM) double cyclization catenane synthesis. Importantly, the naphthalene spacer unit of precursor $\mathbf{6}^+$ not only serves as a rigid linker, but also has the potential to act as a fluorescent reporter group for catenane host anion sensing.

Precursor compound $\mathbf{6}^+\cdot\mathbf{Br}^-$ was prepared in a stepwise procedure shown in Scheme 1. The reaction of 4-(2-(allyloxy)ethoxy)phenol (**1**)[14] and 2,7-bis(bromomethyl)naphthalene (**2**) in the presence of base produced the bromomethylnaphthalene derivative **3** in 31% yield. Alkylation of bromoimidazole **4**[15] with **3** under basic conditions gave **5** in near quantitative yield. The coupling of **5** and **3** afforded the desired bis-vinyl appended precursor $\mathbf{6}^+\cdot\mathbf{Br}^-$ in a yield of 60%

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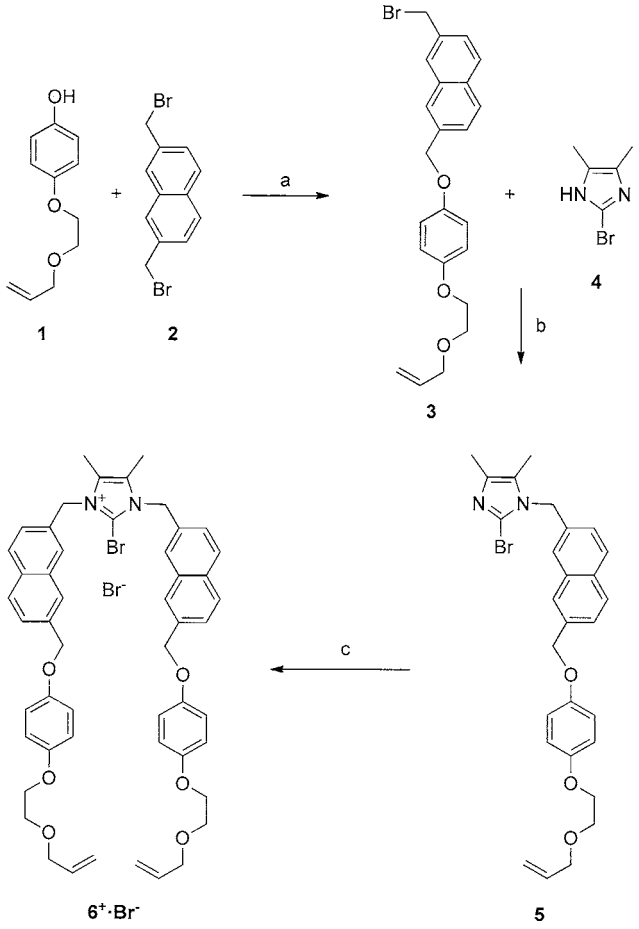


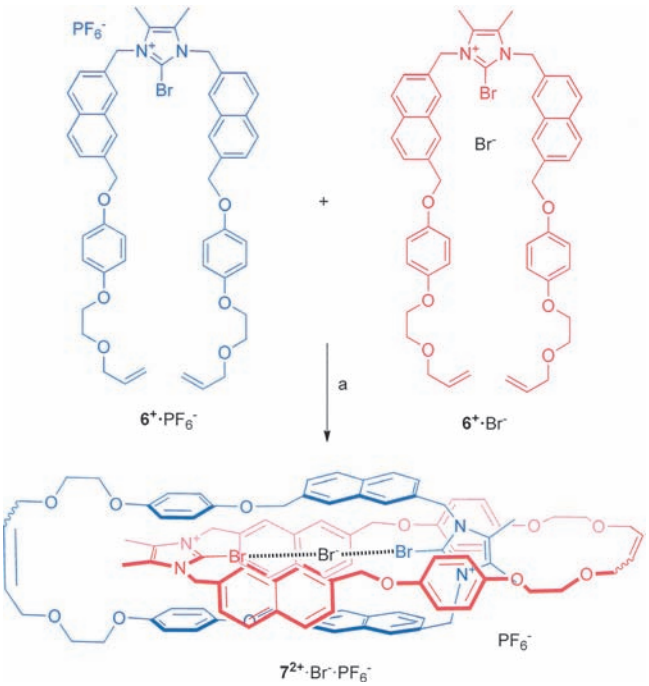
Scheme 1. Synthesis of acycle precursor $\mathbf{6}^{+}\cdot\mathbf{Br}^{-}$. Reagents and conditions: a) K_2CO_3, acetonitrile, RT, 16 h (31%); b) NaOH (1 M in water), acetonitrile, RT, 16 h (98%); c) **3**, acetonitrile, 60°C, 48 h (60%).

(Scheme 1), and anion exchange with NH_4PF_6 (aq) gave the corresponding hexafluorophosphate salt $\mathbf{6}^{+}\cdot\mathbf{PF_6}^{-}$.

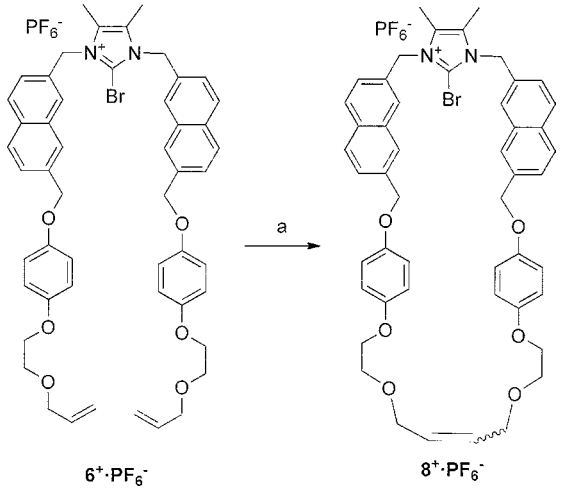
Catenane $\mathbf{7}^{2+}$ was synthesized by RCM reaction of equimolar amounts of the Br^- and PF_6^- salts of $\mathbf{6}^{+}$ in dichloromethane, using Grubbs' 2nd generation catalyst (10 wt%). The catenane $\mathbf{7}^{2+}\mathbf{Br}^{-}\cdot\mathbf{PF_6}^{-}$ was isolated by silica gel preparatory thin layer chromatography in 24% yield (Scheme 2). Bromide anion template removal was achieved by the addition of a saturated aqueous solution of NH_4PF_6 to $\mathbf{7}^{2+}\cdot\mathbf{Br}^{-}\cdot\mathbf{PF_6}^{-}$ in acetonitrile to afford the catenane $\mathbf{7}^{2+}\cdot\mathbf{2\,PF_6}^{-}$ in almost quantitative yield.

It is noteworthy that the bromide anion template was found to be crucial to the synthesis of the XB catenane. Repeating the RCM reaction by using $\mathbf{6}^{+}\cdot\mathbf{PF_6}^{-}$ in the presence of 10 wt% Grubbs' 2nd generation catalyst in dichloromethane gave only the macrocycle $\mathbf{8}\cdot\mathbf{PF_6}^{-}$ which was isolated in 25% yield by silica gel preparatory thin layer chromatography (Scheme 3).

Both catenane $\mathbf{7}^{2+}$ and macrocycle $\mathbf{8}^{+}$ were characterized by ^1H and ^{13}C NMR spectroscopy and high resolution mass spectrometry. The high resolution mass spectra reveal that the isotopic distribution of the macrocycle $\mathbf{8}^{+}$ $[M^+]$ and the catenane $\mathbf{7}^{2+}$ $[M^{2+}]$ are in good agreement with their simulated spectra and the peak corresponding to $\mathbf{7}^{2+}\cdot\mathbf{PF_6}^{-}$



Scheme 2. Synthesis of XB catenane $\mathbf{7}^{2+}\cdot\mathbf{Br}^{-}\ \mathbf{PF_6}^{-}$. Reagents and conditions: a) Grubbs' 2nd generation catalyst (10 wt%), dichloromethane, RT, 16 h (24%).



Scheme 3. Synthesis of the macrocycle $\mathbf{8}^{+}\cdot PF_6^-$. Reagents and conditions: 1) Grubbs' 2nd generation catalyst (10 wt%), dichloromethane, RT, 16 h (25%).

$[M^{2+} + PF_6^- = 1825.5012]$ was also detected (see Supporting Information).

Crystals of $\mathbf{8}^{+}$ suitable for single-crystal X-ray structural analysis were grown by the slow evaporation of an aqueous solution of the chloride/bromide salt of the macrocycle. The asymmetric unit contains two monocationic macrocycles as well as one bromide, one chloride counterion and several water solvates (see Supporting Information). The bromoimidazolium rings are twisted out of the plane of the macrocycle (Figure 2).

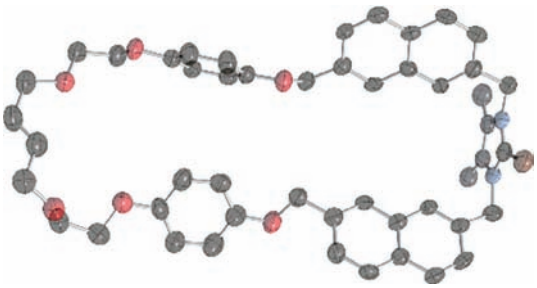


Figure 2. Solid state structure of macrocycle $\mathbf{8}^{+}$. Counterions and hydrogen atoms are omitted for clarity; ellipsoids are shown at 50% probability. Colour scheme: gray = carbon, blue = nitrogen, red = oxygen, brown = bromine.

Comparison of the ^{1}H NMR spectra in CD_3CN of the catenane salts $\mathbf{7}^{2+}\cdot\mathbf{Br}^{-}\cdot\mathbf{PF_6}^{-}$ and $\mathbf{7}^{2+}\cdot\mathbf{2\,PF_6}^{-}$ with macrocycle $\mathbf{8}^{+}\cdot\mathbf{PF_6}^{-}$ provides evidence of the interlocked nature of the catenane (Figure 3).

Importantly the hydroquinone protons of the macrocycle (Figure 3a) have split significantly in the catenane (Figure 3b) with hydroquinone protons *g* moving upfield which is indicative of π–π stacking interactions between the bromoimidazolium groups of one ring and the hydroquinone ring of the other.

In addition the naphthalene protons *j*, *k*, *m*, and *n* of the catenane are shifted upfield in comparison with the same protons of the macrocycle and there is a large downfield shift in the naphthalene proton *i* suggesting the proximity of the bound bromide. Upon exchange to the hexafluorophosphate salt of the catenane (Figure 3c), there is an upfield shift of the naphthalene proton *i*, due to the removal of the bromide anion template. However, the hydroquinone protons *g* and *h* remains split and the naphthalene protons *j*, *k*, *m*, and *n* stay upfield, which suggests that the respective co-conformations of the catenane salts are similar.[16]

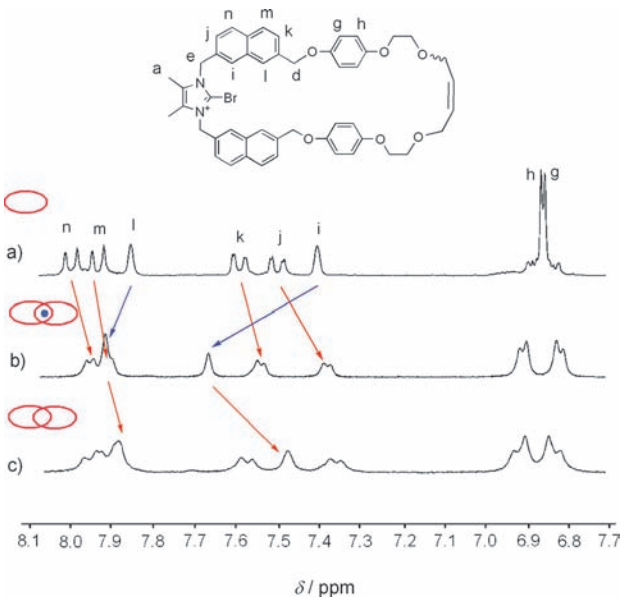


Figure 3. Comparison of the ^{1}H NMR spectra in CD_3CN at 20 °C of the a) macrocycle $\mathbf{8}^{+}\cdot\mathbf{PF_6}^{-}$, b) catenane $\mathbf{7}^{2+}\cdot\mathbf{PF_6}^{-}\cdot\mathbf{Br}^{-}$, and c) catenane $\mathbf{7}^{2+}\cdot\mathbf{2\,PF_6}^{-}$.

The anion recognition properties of the XB catenane $\mathbf{7}^{2+}\cdot\mathbf{2\,PF_6}^{-}$ and macrocycle $\mathbf{8}^{+}\cdot\mathbf{PF_6}^{-}$ were investigated by fluorescence spectroscopy. Catenane $\mathbf{7}^{2+}\cdot\mathbf{2\,PF_6}^{-}$ exhibits one broad and structureless emission band at $\lambda = 309$ nm in CH_3CN ($c = 1\times10^{-5}$ M), exciting at $\lambda = 280$ nm, which is attributed to the monomer emission of the naphthalene motif. The macrocycle $\mathbf{8}^{+}\cdot\mathbf{PF_6}^{-}$ ($c = 1\times10^{-5}$ M in CH_3CN, $\lambda_{exc} = 280$ nm) displays two emission bands at $\lambda = 309$ nm, assigned to the monomer emission, and $\lambda = 425$ nm characteristic of the excimer emission of the naphthalene.[17]

The addition of increasing amounts of F^-, Cl^-, Br^-, I^-, AcO^-, $H_2PO_4^-$, NO_3^- as tetrabutylammonium (TBA) salts and HCO_3^- as tetraethylammonium (TEA) salt to macrocycle $\mathbf{8}^{+}\cdot\mathbf{PF_6}^{-}$ ($c = 1\times10^{-5}$ M in CH_3CN) caused no significant perturbation in the emission spectra of the macrocycle (see Supporting Information). By contrast the addition of Cl^- and Br^- to catenane $\mathbf{7}^{2+}\cdot\mathbf{2\,PF_6}^{-}$ ($c = 1\times10^{-5}$ M in CH_3CN) showed a progressive decrease of the intensity of the emission band located at $\lambda = 309$ nm concomitant with the appearance and increase of a new broad band at $\lambda = 445$ nm (Figure 4a). The

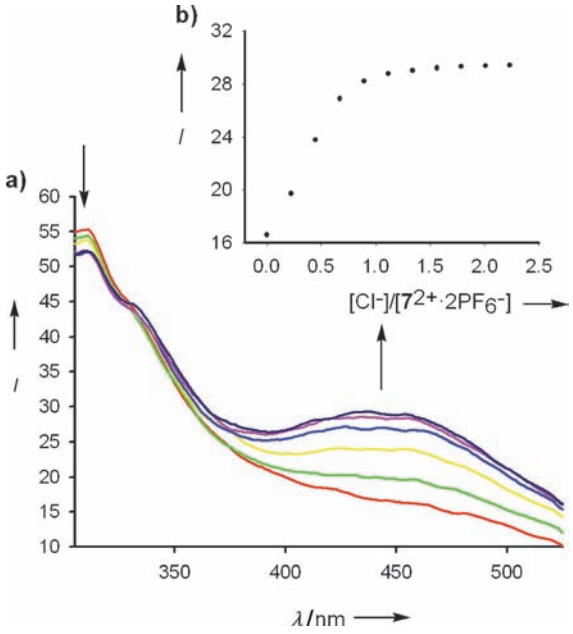


Figure 4. a) Changes in the emission spectra of the catenane $\mathbf{7}^{2+}\cdot2PF_6^-$ (1×10^{-5} M in CH_3CN) upon the addition of increasing amount of Cl^-; b) Changes of emission at 445 nm upon addition of Cl^-.

titration profiles revealed a 1:1 catenane/anion stoichiometry (Figure 4b) and association constants were determined using Specfit[18] (Table 1). Both Cl^- and Br^- are bound strongly, with the smaller halide anion being preferentially complexed by a significant factor of 25-times. Remarkably the addition of excess amounts of F^-, I^-, AcO^-, $H_2PO_4^-$, NO_3^-, and HCO_3^- to a solution of the catenane $\mathbf{7}^{2+}\cdot\mathbf{2\,PF_6}^{-}$ caused no significant perturbations of the interlocked host's emission spectrum (see Supporting Information). This suggests the unique preorganized interlocked cavity of catenane $\mathbf{7}^{2+}$ is of exclusive

Table 1: Association constants K_a for catenane $7^{2+}\cdot 2\,PF_6^-$ with different anions in CH_3CN at 20 °C.

Receptor	Anion[a]	K_a [M^{-1}][b]
$7^{2+}\cdot 2PF_6^-$	F^-	NB[c]
	Cl^-	3.71×10^6
	Br^-	1.48×10^5
	I^-	NB
	AcO^-	NB
	$H_2PO_4^-$	NB
	NO_3^-	NB
	HCO_3^-	NB

[a] Anions have been used as tetrabutylammonium salts, except HCO_3^-, which was added as a tetraethylammonium salt. [b] Error < 10%. [c] NB: No evidence of binding.

complementary size for recognition of Cl^- and Br^- anions through intra-ring cooperative XB bromoimidazolium–halide interactions.

Molecular dynamics (MD) simulations were performed in an explicit acetonitrile solvent model using a suitable structure of catenane $\mathbf{7^{2+}\cdot PF_6^-\cdot Cl^-}$ found by quenched dynamics (see Supporting Information). The MD simulations were carried out with Amber11[19] using the pmemd.cuda AMBER executable, able to accelerate explicit solvent Particle Mesh Ewald (PME) calculations through the use of GPUs.[20] Halogen bonding is not described by the standard force field parameters, but recently two similar additions to the General Amber Force Field (GAFF)[21] were proposed to describe this interaction.[22,23] We followed a similar approach and parameterized a dummy atom (DU) optimally located at a Br–DU distance of 2.3 Å. Three MD runs of 30 ns each were performed in a NPT ensemble leading to a total of 90 ns sampling time. The remaining simulation and parameterization details are given in the Supporting Information. A representative snapshot of the three replicas was extracted by clustering the MD trajectories and is represented in Figure 5.

Two simultaneous halogen bonds are established between the bromine atoms of both macrocycles and the chloride anion. Furthermore, the π–π stacking interaction between one hydroquinone and a naphthalene group was also observed throughout the course of MD simulation as illustrated with this particular snapshot. Also, one bromoimidazolium unit is stacked over another hydroquinone group.

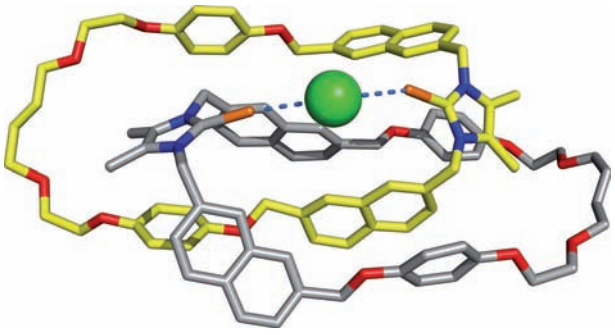


Figure 5. Representative co-conformation of $\mathbf{7^{2+}\cdot PF_6^-\cdot Cl^-}$ in acetonitrile solution. Hydrogen atoms, solvent molecules, and $\mathbf{PF_6^-}$ counterion were omitted for clarity. The two CBr···Cl^- halogen bonds are drawn as light blue dashed lines. Color scheme: yellow or gray = carbon, red = oxygen, blue = nitrogen, brown = bromine, green = chloride.

The stability of the halogen bonded assembly in the catenane system was accessed by monitoring both the Br···Cl^- distances and the C-Br···Cl^- angles, since the halogen bonds are characterized by short and almost linear contacts. The histograms built with 3×30 ns data were projected on a 2D surface and are shown in the Supporting Information (Figure S24) for both macrocycles. The areas with larger densities (red) are located at Br···Cl^- = 3.4 Å and C–Br···Cl^- = 172.5°, which in addition to the relatively narrow area of the density maxima, is consistent with the continuous presence of two simultaneous Br···Cl^- halogen bonds.

In conclusion, the first halogen-bonding catenane has been prepared by bromide anion templation. Upon removal of the bromide anion template, fluorescence spectroscopic investigations reveal the catenane host system to bind strongly and sense selectively chloride and bromide, where impressively, no significant optical response is detected with F^-, I^-, AcO^-, $H_2PO_4^-$, and HCO_3^- anions. These observations indicate the unique, preorganized topological nature of the catenane host cavity facilitates the efficacy of cooperative XB recognition of chloride and bromide guest species. The incorporation of XB donor groups into interlocked host structural frameworks is continuing in our laboratories.

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