Supramolecular Chemistry

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A Halogen-Bonded Dimeric Resorcinarene Capsule**

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Abstract: *Iodine (I_2) acts as a bifunctional halogen-bond donor connecting two macrocyclic molecules of the bowl-shaped halogen-bond acceptor, N-cyclohexyl ammonium resorcinarene chloride **1**, to form the dimeric capsule [(1,4-dioxane)$_3$@**1**$_2$(I_2)$_2$]. The dimeric capsule is constructed solely through halogen bonds and has a single cavity (V = 511 Å^3) large enough to encapsulate three 1,4-dioxane guest molecules.*

Hydrogen bonds (HB) are weak interactions that are extensively used in the design of organic supramolecular assemblies.[1] Their application spans from the preparation of simple compounds to complex materials and those mimicking biological processes.[2] The halogen bond (XB) is analogous to HB in strength and directionality, and has recently been defined.[3] This noncovalent interaction is based on a polarized halogen atom which interacts with a Lewis base, in some cases with coordinative[4] or covalent character, to form a XB.[3] The XB donors exhibit an anisotropic electron distribution leading to an electropositive region on the halogen atom named the σ hole.[5] The strength of the XB interactions (R−X···A) usually follow the trend X = I > Br ≫ Cl ≫ F. Dihalogens (X_2) are very interesting XB donors and often display very short XB distances, sometimes approaching those of the corresponding covalent bonds.[6] Though the polarizability of the halogen in an XB donor is critical, the strength of the X_2···A-type XB can be correlated to the ability of A to accept a halogen bond[7] as a Lewis base[8] leading to a "basicity scale" for I_2···A halogen bonds.

Anions which are Lewis bases are good hydrogen- and halogen-bond acceptors.[7,9] The ability of anions to have multiple coordination geometries has led to their utilization in numerous noncovalent interactions.[10] Halides are spherical, symmetrical anions with the negative charge concentrated on a single atom making them excellent HB and XB acceptors.[9,10] As a result of these properties[11] halides have coordination numbers, that is, the number of hydrogen or halogen bonds, ranging typically from four to eight. If simultaneously present, both HB and XB can therefore be used in tandem to form functional assemblies.[12] Multiple 1D, 2D, and 3D halogen-bonded structures with halides have been reported.[13]

The design and synthesis of components for capsular assemblies with internal cavities capable of specific guest encapsulation is a very topical area of supramolecular chemistry.[1] Molecular compounds, such as calixarenes[14] and resorcinarenes,[15] with preorganized cavities composed of aromatic groups provide an electron-rich interior that can bind a variety of guests through cation···π and CH···π interactions. Some of the most iconic dimeric capsules are those from Rebek et al.[16] where a urea-functionalized resorcinarene cavitand forms very stable dimeric capsular assemblies through hydrogen bonding, simultaneously entrapping one or more guest molecules within the confined space. The *N*-alkyl ammonium resorcinarene halides (NARXs),[17] hydrogen-bonded analogues of covalent cavitands,[18] are a family of host compounds recently developed by us.[17] NARXs are a subset of resorcinarenes where the strong intramolecular hydrogen bonds between the halides and the ammonium groups leads to a cavitand-type structure.[17] The NARXs are intramolecular salt molecules with four spatially fixed halogen-bond acceptor sites (the four anions) with a deep cavity for guest binding. The resorcinarene skeleton and the strong hydrogen-bond interactions from the ammonium ions shield the halide anions, so that in the presence of suitable XB donors, the XB interactions can only occur parallel to the upper rim of the NARXs or perpendicular to it. In such an assembly, the interior of the cavity is preserved for guest binding.[17] We have recently shown that NARXs are excellent XB acceptors and form halogen-bonded deep-cavity cavitands with specific XB donors.[19] To date, there are no reported dimeric capsules constructed solely from halogen bonds. Our previous attempts to obtain solely halogen-bonded capsular assemblies with either the NARXs as XB acceptors[19] or iodoethynylresorcinarene cavitands as XB donors[20] have not been successful.

Herein, we present the first example of a solely halogen bonded dimeric capsule, [(1,4-dioxane)$_3$@**1**$_2$(I_2)$_2$], formed between two *N*-cyclohexyl ammonium resorcinarene chloride (**1**) macrocycles as the XB acceptors and two iodine molecules as the XB donors (Figure 1). This dimeric capsule has a cavity that encapsulates three well-ordered 1,4-dioxane molecules.

The ring opening of the tetrabenzoxazine in the presence of hydrochloric acid under refluxing conditions results in the formation of **1** (see the Supporting Information).[17] The hydrogen bonds between the ammonium moieties and the chloride anions form a strong circular seam (···NArRH_2^+···Cl^-···)$_4$ creating a cavity with size and shape analogous to covalent resorcinarene cavitands.[19,21]

Slow evaporation of a 1:4 mixture of **1** and I_2 in chloroform with a few drops of 1,4-dioxane resulted in the form-

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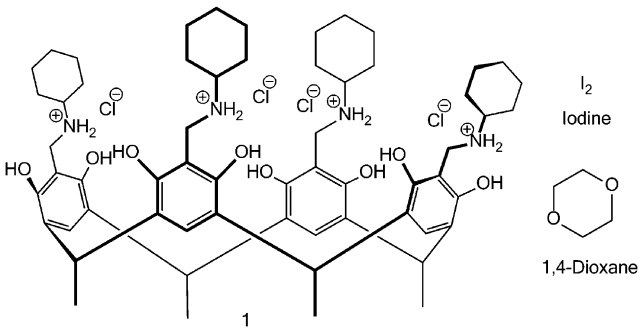

Figure 1. The host **1** (XB acceptor), I_2 (XB donor), and 1,4-dioxane (guest).

ation of single crystals of the seven-component assembly [(1,4-dioxane)$_3$@**1**$_2$(I_2)$_2$] (Figure 2) which were analyzed by X-ray crystallography. The supramolecular assembly consists of two molecules of **1** connected by two I_2 molecules through

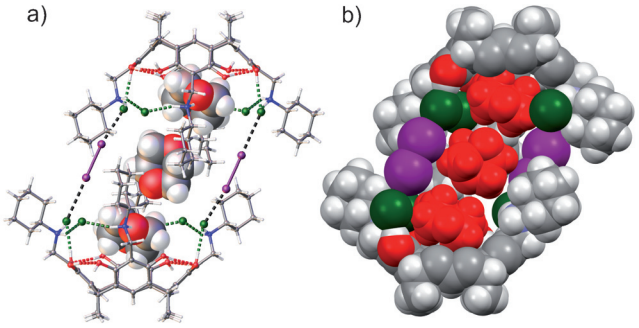

Figure 2. Representation of the halogen-bonded dimeric capsule [(1,4-dioxane)$_3$@**1**$_2$(I_2)$_2$] with three 1,4-dioxane molecules in the cavity. a) Ball-and-stick model of the capsule with the 1,4-dioxane guests as space-filling CPK models. The XBs are shown in black and HBs in green and red dotted lines. b) A sliced space-filling CPK plot of the halogen-bonded capsule highlighting the I···Cl XBs. Atom colors: C = gray; H = white; N = blue; O = red; Cl = green; I = purple. In (b), the encapsulated 1,4-dioxane molecules are shown in red.

moderately strong XBs, which are further extended by additional XBs along the *a* direction (Figure 3) and by intercapsular HBs along the [101] direction (see the Supporting Information). The dimeric capsule entraps three 1,4-dioxane molecules in its cavity. Additionally, one of the chlorides is involved in halogen bonding to a third I_2 molecule, which does not play a role in the capsule formation, but bridges the capsules together in the solid state. In such a way, a halogen-bonded square-shaped $[Cl_4I_{12}]^{4-}$ structural unit is formed (Figure 3).

As expected, host **1** stabilizes its bowl conformation through moderate O–H···O, O–H···Cl$^-$, and N–H···Cl$^-$ hydrogen bonds. The encapsulation of the 1,4-dioxane guest helps the formation of the dimeric capsule by restricting H bonds to two of the four chlorides (Figure 2a), consequently leaving these Cl$^-$ ions available for halogen bond formation. When the two capsule halves meet, the rest of the cavity is filled by the third 1,4-dioxane molecule. The volume[22] of the cavity is 511 Å^3 and as the volume of the

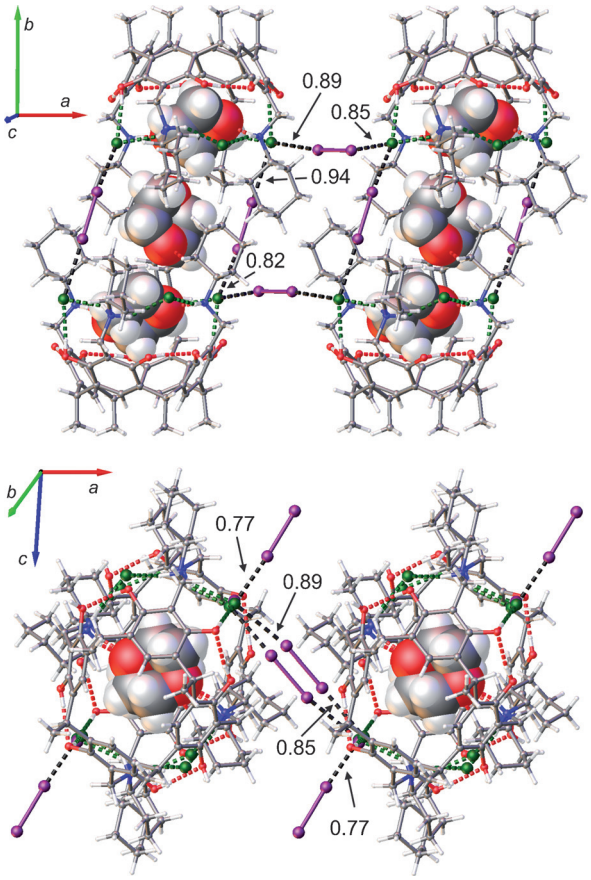

Figure 3. Adjacent capsules connected by a [I–I···Cl$^-$···I–I···Cl$^-$···I–I···]$_2$ XB network shown in the *ab* (top) and the *ac* (bottom) planes. Numbers given indicate the halogen-bonding ratio R_{XB}. Atom colors: C = gray; H = white; N = blue; O = red; Cl = green; I = purple.

1,4-dioxane is 94.1 Å^3, thus 3 × 94.1 Å^3/511 Å^3 gives the packing coefficient as 55.2%, a perfect match with the optimal value of 55% ± 0.09 as defined by Mecozzi and Rebek.[23] The halogen-bonding ratio R_{XB} ($R_{XB} = d_{XB}/(X_{vdw} + B_{vdw})$) can be used to roughly measure the strength of the XB interactions, where d_{XB} is the halogen-bonding distance and X_{vdw} and B_{vdw} are the van der Waals radii of each of the two components of the halogen bond.[24] In this capsule the R_{XB} values range from 0.77 to 0.94 (Figure 3).

All previous attempts to directly construct halogen-bonded dimeric capsules with an interior cavity for guest binding have been focused on using strong organic XB donors or acceptors.[20,25] The nature of the XBs involving organic donors differ from that involving inorganic donors.[26] Halogen bonds with organic donors are usually regarded to be largely electrostatic in nature, whereas charge-transfer interactions dominates the inorganic XB type. Regardless of the nature of the XBs, the obvious advantages of using I_2 as an XB donor to build dimeric capsules are its small size, linearity, and the bifunctionality of the XB interactions. Each of these characteristics are useful to stabilize spherical or ellipsoidal assemblies. The other advantage is that as the XB donor I_2 does not have additional interfering substituents which might sterically block the cavity or render the dimeric capsule formation impossible.

As a result of solvent interference, it is challenging to unambiguously demonstrate halogen bonding in solution. However, NMR spectroscopy has been shown to be a reliable tool to study XB in solution.[27] The chloride ions in **1** are hydrogen bonded to the ammonium and hydroxy groups. When these anions are involved in halogen bonds, the electronic environment of the -OH and -NH_2 protons reflect these interactions in a synergistic manner. This strategy has proven to be successful in previous NMR studies,[19,28] where the chemical-shift changes indicated that these large neutral organic salts can bind guest molecules, such as 1,4-dioxane, low-molecular-weight alcohols, as well as *N*-alkyl and *N*-aryl acetamides in chloroform.[17,19,28] Therefore, the ^{1}H NMR measurements were carried out to investigate if a halogen-bonded assembly between **1** and I_2 can be detected in solution.

For the NMR experiments, several samples containing **1** (20 mM) as XB acceptor, I_2 as XB donor, and 1,4-dioxane as the guest, were prepared and their ^{1}H NMR spectra were recorded at 303 K. The ^{1}H NMR spectra shows changes in signals attributable to the -OH and -NH_2 protons of the host **1**. These changes are attributed to the formation of XB in solution (Figure 4). The changes in the -NH_2 signals of the host **1**, range from $\Delta\delta = 0.1$ to 0.2 ppm, which correlates with

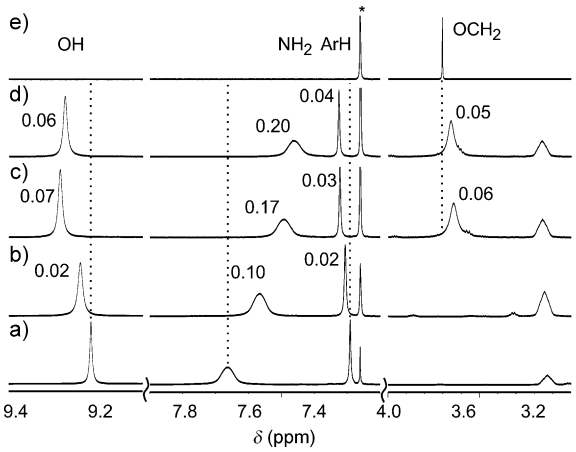

Figure 4. The ^{1}H NMR spectra in $CDCl_3$ at 303 K of: a) **1** (20 mM); b) 1:1 mixture of **1** and I_2; c) 1:3:1.5 mixture of **1**, I_2, and 1,4-dioxane; d) 1:excess:1.5 mixture of **1**, I_2, and 1,4-dioxane; e) 1,4-dioxane (20 mM). Dashed lines and values (in ppm) give an indication of the chemical-shift changes from signals attributable to the pure host (a) and guest (e).

the amount of added I_2. In the presence of 1,4-dioxane, significant complexation-induced upfield shifts in the ^{1}H NMR resonance signals for the 1,4-dioxane protons were detected (Figure 4), which revealed the strong host–guest binding. I_2 is a strong monofunctional XB donor, but can also act as a weak bifunctional XB donor. After the formation of the first XB bond ($Cl^{-}\cdots I(a)–I(b)$), and because of the charge-transfer interactions, the XB donor ability of the second iodine atom I(b) is greatly decreased and can usually be detected in extremely high concentrations in solution or more typically in the solid state as [$Cl^{-}\cdots I(a)–I(b)\cdots Cl^{-}$].[29] Halogen bonding is very labile in solution[27] and such bifunctional assembly is virtually impossible to detect at low concentrations (within the solubility limit of the compounds) using NMR spectroscopy.

In summary, we present the first example of a solely halogen-bonded dimeric capsule in the solid state. In this seven-component assembly both XB and HB are working concertedly to form a stable network of noncovalent interactions stabilizing the capsular structure. The formed capsule has a cavity volume of 511 Å^3 which is perfectly sized for the entrapment of three 1,4-dioxane molecules. Prior to this work, the construction of a directly halogen-bonded dimeric capsule had been unsuccessful even though the structurally similar hydrogen-bonded and metal-ion-mediated analogues are known.[30] Molecular I_2 acts as a bifunctional XB donor and connects the two hosts through $Cl^{-}\cdots I–I\cdots Cl^{-}$ halogen bonds to form a capsular entity. The entrapped 1,4-dioxane guest molecules are fixed in the cavity by the NH$\cdots$O hydrogen bonds. The ^{1}H NMR spectroscopic studies in chloroform clearly confirm the existence of iodine-to-resorcinarene salt halogen bonding in solution. The dimeric capsule itself was not directly detected in solution as result of the weakness of the second $I\cdots Cl^{-}$ halogen bond (in the solid state $R_{XB} = 0.82$ for the first $I\cdots Cl^{-}$ XB, and $R_{XB} = 0.94$ for the second $I\cdots Cl^{-}$ XB). Marked chemical shift changes in the -NH_2 proton signals with increased I_2 concentration are detected ($\Delta\delta =$ 0.1–0.2 ppm, Figure 4)and are significantly larger than those reported for halogen-bonded deep cavitands with bromotrichloromethane ($\Delta\delta = 0.01$–0.03 ppm).[18] Our results highlight the truly versatile nature of the NARXs as receptor molecules and supramolecular building blocks and have opened up the possibility to utilize halogen bonding in the construction of other capsular assemblies with cavities suitable for a variety of guest compounds. We are currently studying the stability and guest-binding properties of these capsular assemblies and are investigating the possibility to build stable and even larger assemblies through halogen bonding.

Experimental Section

The host **1** was synthesized according to reported procedures.[17] Iodine and 1,4-dioxane were commercially available. ^{1}H NMR spectra were recorded on a Bruker Avance DRX 500 MHz spectrometer. Single crystals of the dimeric capsular complex [(1,4-dioxane)$_3$@**1**$_2$(I_2)$_2$] were obtained by slow evaporation of the chloroform solution containing a 1:4 mixture of resorcinarene chloride **1**:I_2 in the presence of 1,4-dioxane. The crystal was measured at 123 K using an Agilent SuperNova dual wavelength diffractometer with a micro-focus X-ray source and multilayer optics monochromatized Mo-$K\alpha$ ($\lambda = 0.71073$ Å) radiation (see the Supporting Information for detailed crystallographic information). CCDC-1003004 [(1,4-dioxane)$_3$@**1**$_2$(I_2)$_2$] 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.

Keywords: halogen bonds · hydrogen bonds · resorcinarenes · self-assembly · supramolecular chemistry

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