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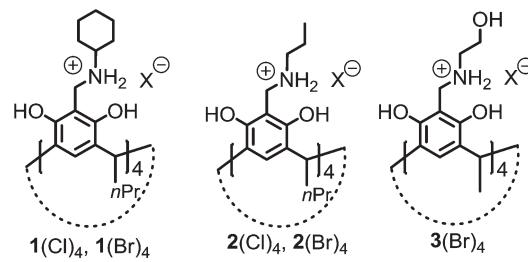
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Halogen bonding,<sup>1</sup> as a non-covalent interaction, is analogous to hydrogen bonding in both strength and directionality. Halogen bonding is widely used in the design and construction of small and large supramolecular assemblies with novel applications in crystal engineering, materials science and biological systems.<sup>2–8</sup> Within the broad area of halogen bonding, polyhalides assembled through halogen···halogen interactions are particularly interesting. Charge transfers between the halides and the molecular halogen stabilize the polyhalide species and endow the final polyhalides with potential electronic and photophysical properties.<sup>9–11</sup>

The chemistry of *N*-alkyl ammonium resorcinarene halides (NARXs) as receptors and supramolecular synthons has been recently developed.<sup>12</sup> The bowl-shaped  $C_{4v}$  symmetry of the resorcinarene core in the NARXs is maintained by intramolecular hydrogen bonds between adjacent hydroxyl groups. The large organic salt molecules feature a hydrogen bonded cyclic geometry with the aromatic groups providing the pre-organized deep electron-rich interior cavities. The halides in the circular hydrogen bond seam ( $(\cdots \text{NArRH}_2^+ \cdots \text{X}^- \cdots)_4$ ) with hydrogen and halogen bond acceptor ability introduce the possibility of extending the cavity size in the presence of suitable donors.<sup>13</sup> This broadens the ability of the NARXs to act as receptors for a larger variety of guest molecules as well as increases their potential as synthons for larger supramolecular networks and assemblies.<sup>13</sup> Molecular iodine ( $\text{I}_2$ ) as a halogen bond donor was successfully used to construct a halogen-bonded dimeric capsule with an NARX, where  $[\text{Cl} \cdots \text{I} \cdots \text{Cl}]^{2-}$  species was detected in the solid state as the

main factor linking the two capsule halves.<sup>9</sup> To further investigate the nucleophilicity of the halides in NARXs towards  $\text{I}_2$ , in this contribution,  $\text{I}_2$  was introduced into four NARXs: *N*-cyclohexyl ammonium resorcinarene chloride (**1(Cl<sub>4</sub>)**) and bromide (**1(Br<sub>4</sub>)**), *N*-propyl ammonium resorcinarene chloride (**2(Cl<sub>4</sub>)**) and bromide (**2(Br<sub>4</sub>)**), and the water soluble *N*-ethanol ammonium resorcinarene bromide (**3(Br<sub>4</sub>)**) (Scheme 1). Surprisingly, triiodide anions were observed from the mixture of  $\text{I}_2$  with **1(Cl<sub>4</sub>)**, **1(Br<sub>4</sub>)** and **2(Br<sub>4</sub>)**, while the rare linear pentaiodide anion was detected in the system containing  $\text{I}_2$  and **3(Br<sub>4</sub>)** in MeOH.

Crystals of 1,4-dioxane@**1(Cl<sub>3</sub>·I<sub>3</sub>)** were obtained by slow evaporation of the methanol solution from a 1:2 molar mixture of **1(Cl<sub>4</sub>)** and  $\text{I}_2$  in the presence of 1,4-dioxane. Unlike in the reported capsular assembly between an analogue of **1(Cl<sub>4</sub>)** with a shorter lower rim in which three ordered 1,4-dioxane molecules were entrapped in the cavity with the  $[\text{Cl} \cdots \text{I} \cdots \text{Cl}]^{2-}$  species stabilizing the two capsule halves, in the new assembly, a stable triiodide ( $\text{I}_3^-$ ) anion was formed, which replaced one of the chlorides from the cation–anion seam. The triiodide does not form part of the cation–anion hydrogen-bonded seam; instead, it is located above the resorcinarene skeleton. The bowl shape of the resorcinarene frame is still preserved with one 1,4-dioxane molecule trapped in the cavity *via* two N–H···O hydrogen bonds, although only two chlorides are positioned in the cation–anion seam. However, due



Scheme 1 The *N*-alkyl ammonium resorcinarene halides (NARXs) (**1(X<sub>4</sub>)**–**3(X<sub>4</sub>)**).

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to the steric hindrance between the large  $I_3^-$  and the four *N*-cyclohexyl ammonium arms, one of the arms rotates 180° with the ammonium hydrogens pointing outwards and is hydrogen-bonded to one additional *exo*-1,4-dioxane molecule (Fig. 1A). The *exo*-cavity-1,4-dioxane molecule simultaneously hydrogen bonds to two adjacent resorcinarene molecules forming a dimer ( $[1,4\text{-dioxane}@\{1(\text{Cl}_3\text{-}I_3)\}] \cdot 1,4\text{-dioxane} \cdot [1,4\text{-dioxane}@\{1(\text{Cl}_3\text{-}I_3)\}]$ ) (Fig. 1C). In addition to the linkage of 1,4-dioxane, the dimer is also connected by the third  $\text{Cl}^-$  and a disordered water molecule *via* multiple hydrogen bonds (Fig. 1C). Along the crystallographic *b*-axis, the resorcinarene framework is arranged in a head-to-tail manner, with the  $I_3^-$  squeezing into the space between the upper rim of one resorcinarene and the lower rim of another. This kind of arrangement causes two of the four propyl groups at the lower rim to fold in *gauche* conformation. Intermolecular O–H···O hydrogen bonds are responsible for the structural extension along the *a*-axis (Fig. S1†).

The formation of the triiodide anion in the structure  $1,4\text{-dioxane}@\{1(\text{Cl}_3\text{-}I_3)\}$  is unexpected. We assume that it is the result of the heterolytic dissociation of  $I_2$  in the presence of an electron donor of either  $\text{Cl}^-$  or the solvent methanol molecule. The produced  $I^-$ , further interacts with one  $I_2$  molecule giving rise to the  $I_3^-$  anion (Scheme 2). It is noteworthy that the difference between triiodide and chlorodiiodide is evident from the difference Fourier map; therefore, the species of  $I_3^-$  can undoubtedly be confirmed by single crystal X-ray analysis.

To further investigate this process, we extended the study to  $1(\text{Br}_4)$ , an analogue of  $1(\text{Cl}_4)$ , and to the more flexible *N*-propyl groups  $2(\text{Cl}_4)$  and  $2(\text{Br}_4)$ . Single crystal analysis of  $1(\text{Br}_4)$ , which is the bromide analogue of  $1(\text{Cl}_4)$ , reveals an isomeric structure ( $1,4\text{-dioxane}@\{1(\text{Br}_3\text{-}I_3)\}$ ). The single crystals were obtained by slowly evaporating the methanol solvent from the 1:2 mixture of  $1(\text{Br}_4)$  and  $I_2$  under the same conditions as for  $1(\text{Cl}_4)$  (Fig. 1B). Unfortunately, we could not isolate any suitable single crystals from the reaction of  $2(\text{Cl}_4)$  with  $I_2$ . However, the reaction of the bromide analogue  $2(\text{Br}_4)$

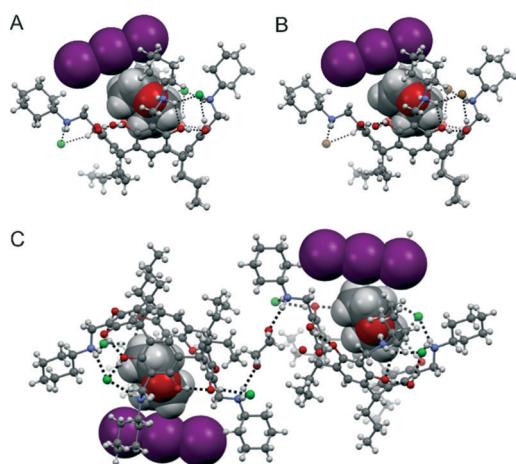
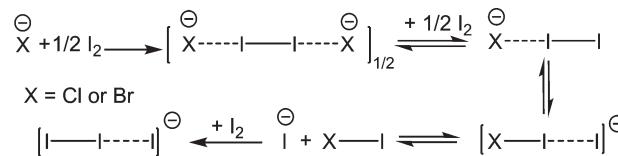


Fig. 1 The structural units in  $1(\text{Cl}_3\text{-}I_3)$  (A) and  $1(\text{Br}_3\text{-}I_3)$  (B) as well as the dimer  $[1,4\text{-dioxane}@\{1(\text{Cl}_3\text{-}I_3)\}] \cdot 1,4\text{-dioxane} \cdot [1,4\text{-dioxane}@\{1(\text{Cl}_3\text{-}I_3)\}]$  (C).



Scheme 2 The proposed process of the formation of triiodide in the system.

with  $I_2$  resulted in a self-included dimer with six bromides and two triiodides.

The formation of the self-included dimer is not unusual. We have previously reported a self-included dimeric assembly of other *N*-propyl ammonium halides.<sup>12a,14</sup> Usually, one of the *N*-propyl ammonium arms from one NARX resides in the cavity of the second molecule with the help of six halide anions, which further bind the two resorcinarene dimer halves *via* multiple inter- and intramolecular hydrogen bonds. In this structure, for each resorcinarene cation, four  $\text{Br}^-$  anions are situated between the ammonium arms, among which two are shared by the two receptors with four  $\text{NH} \cdots \text{Br}^-$  hydrogen bonds for each  $\text{Br}^-$  as depicted in the schematic of Fig. 2A. The other four  $\text{Br}^-$  anions are all involved in one  $\text{OH} \cdots \text{Br}$  and two  $\text{NH} \cdots \text{Br}$  interactions. The dimer formally shows two positive charges, and as a result, two triiodide anions appear in between the four propyl groups at the lower rim. It is worth noting that although 1,4-dioxane was used in the crystal growth process, it was not found in the  $[2(\text{Br}_3\text{-}I_3)]_2$  assembly. The stability of the self-included dimer overrides the possible host-guest binding process of 1,4-dioxane. The formation of

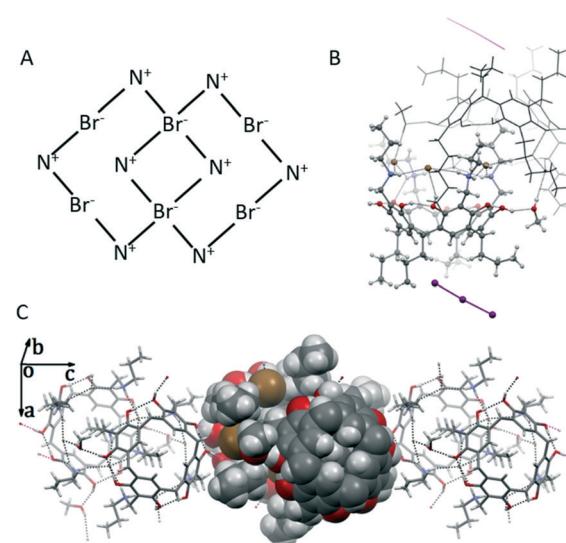


Fig. 2 (A) Schematic representation of the cation-anion hydrogen bond pattern in the self-included dimer. (B) The dimeric structure of  $[2(\text{Br}_3\text{-}I_3)]_2$ ; for clarity, the second NARXs are shown as black lines. (C) The hydrogen-bonded 1D polymer of dimers along the *c* direction with the dimer in the middle in CPK mode. The inter-dimeric hydrogen bonds are shown as violet dashed lines, while the other HBs are shown in black. The lower propyl groups and the triiodides were omitted for clarity.



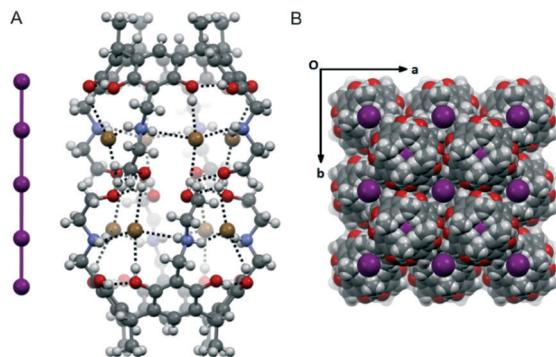


Fig. 3 The hydrogen bonded dimeric capsule in  $[3(\text{Br}_{3.5})]_2 \cdot \text{I}_5$  (A) and its solid state packing in CPK mode (B).

such a dimer involves six of the eight anions, thus releasing the two “free” anions to be involved in the triiodide formation.

In the reaction of NARX  $3(\text{Br}_4)$  with  $\text{I}_2$  in methanol, we surprisingly found a very rare linear  $\text{I}_5^-$  anion in the crystal structure. The water soluble NARX  $3(\text{Br}_4)$  was synthesized according to recently reported procedures.<sup>15</sup> Therein, the chloride analogues were shown to bind a series of alkanes, haloalkanes and arenes in water *via* hydrophobic interactions. The crystal structure of one chloride analogue showed a dimeric capsule with two 1,4-dioxane molecules trapped within the interior cavity similar to Rebek's classical hydrogen bonded cylindrical capsule.<sup>16</sup> Here, the dimeric capsule  $[3(\text{Br}_{3.5})]_2 \cdot \text{I}_5$  is formed in which the two salt molecules are arranged in a staggered pair. The two capsule halves are held together by eight  $\text{OH}^- \cdots \text{Br}$  intermolecular hydrogen bonds. Due to the high symmetry of the structure, each  $\text{Br}^-$  anion has 0.9 occupancy with the whole capsule bearing one positive charge, which is counter-balanced by one  $\text{I}_5^-$  anion. Highly disordered solvent molecules were observed in the cavity of the capsule. In general, the  $\text{I}_5^-$  anion formed can be regarded as an adduct of the  $\text{I}_3^-$  with an additional  $\text{I}_2$ , or  $\text{I}^-$ , and two  $\text{I}_2$  molecules. The structures of the  $\text{I}_5^-$  anion have been intensively reported;<sup>10</sup> however, in most cases, they display a “V” or an “L” shaped geometry. The linear  $\text{I}_5^-$  species is rarely reported.<sup>17,18</sup> In  $[3(\text{Br}_{3.5})]_2 \cdot \text{I}_5$ , the formally centrosymmetric  $\text{I}_5^-$  is considered as a halogen-bonded adduct of  $\text{I}^-$  and two  $\text{I}_2$ , with the central  $\text{I}^- \cdots \text{I}^- \cdots \text{I}$  halogen bond distance of 3.191 Å ( $\times 2$ ,  $R_{\text{XB}} = 0.81$ ; ref. 19) and the terminal I-I length of 2.841 Å ( $\times 2$ ). A strong charge transfer interaction occurs from the  $\text{I}_2$  and the central  $\text{I}^-$  anion, elongating the terminal I-I bonds. The linear geometry of the  $\text{I}_5^-$  here is also due to the molecular packing in the crystal lattice (Fig. 3B).

## Conclusions

In summary, we present four NARX<sub>3</sub>I<sub>n</sub> ( $n = 3$  or 5 and X = Cl or Br) compounds, three triiodides and one with a linear pentaiodide anion. The single crystal X-ray diffraction study confirms that in two *N*-cyclohexyl compounds and one *N*-propyl NARX compound a triiodide anion is formed which

then replaces one of the original halides. The *N*-ethanol NARX  $3(\text{Br}_4)$  resulted in a rare linear pentaiodide entrapped within the crystal lattice. The formation of polyiodides in this system is assumed to be the result of the heterolytic dissociation of  $\text{I}_2$  in the presence of NARX halide anions. The electron donor properties of the NARX halides and/or the solvent methanol molecule are probably responsible for this process. The pentaiodide is described as a halogen bonded adduct of  $\text{I}^-$  and two  $\text{I}_2$ . In addition to their anion exchange properties, this study further highlights that the *N*-alkyl ammonium resorcinarene halides are versatile molecular building blocks for the design and construction of larger supramolecular assemblies.

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