Water−Chloride and Water−Bromide Hydrogen-Bonded Networks: Influence of the Nature of the Halide Ions on the Stability of the Supramolecular Assemblies

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Two compounds, namely, $[TTPH_2](Cl)_2\cdot 4H_2O$ (**1**) and $[TTPH_2](Br)_2\cdot 4H_2O$ (**2**), (TTP = 4′-*p*-tolyl-2,2′:6′,2″-terpyridine) were synthesized from purely aqueous media and characterized by physical techniques. In the solid-state structures of these compounds, interesting supramolecular assemblies are observed. In **1**, an unusual staircase-like architecture of the tape of edge-shared planar water hexamer is of importance, where the chloride ions are at the two edges of the tape. In **2**, the polymeric nature of the water−bromide assembly is of interest, where discrete open-cube water octamers are doubly bridged by bromide ions. Semiempirical and DFT calculations confirm that the nature of the anion indeed affects the topology of the water−halide assemblies. We conclude that the protonated $[TTPH_2]^{2+}$ species can act as appropriate receptors for halide ions, which in turn act as a matrix for the formation of polymeric 1D water−halide assemblies.

1. Introduction

The significance of water in various technological processes including nanoscale assembly,[1] the importance of water in life processes,[2] and a quest to understand its anomalous behavior[3] have incited extensive research on water chemistry. Small water clusters attract considerable experimental[4,5] and theoretical interest[6] because they are the basic structural units of large water assemblies that could help in understanding the structure and properties of bulk water. A clear perception of the cooperative behavior of water molecules leading to the formation of clusters is a prerequisite for unveiling the properties of water.[4]

A number of structurally characterized water clusters in organic[7] and in metal−organic[8] crystalline materials are now known. A variety of water clusters and water polymers of diverse morphologies (1D,[9] 2D,[10] 3D[11]) have been found in various crystal environments as well, and there have been efforts to control water topologies in the context of crystal engineering.[12] In the formation of these clusters, not only do water molecules themselves unite but suitable anions can also take part in the assembly to satisfy the donor−acceptor balance. However, as yet, only a few water−anion clusters[13] have been characterized in the solid state. Understanding the clustering behavior of various anions such as chloride, bromide, nitrate, perchlorate, and so on with water molecules has important bearing for phenomena such as the solvation of the respective salts, the transport of various anions in biological systems, atmospheric aerosol formation, and so on. CSD studies have revealed numerous water clusters[14] as well as water−anion clusters,[15] and it was found that water−anion clusters in many cases assume the same topology as the corresponding water-only clusters. In this submission, water−chloride and water−bromide assemblies of hitherto unknown topologies are presented. These assemblies reveal the effect of changing the halide ions on the assembly of water molecules. The stability of these remarkable supramolecular networks has been theoretically investigated, and the influence of the halides on the self-organization was examined.

2. Experimental Section

All reactions were carried out in water. All reagents were purchased from Sigma or E. Merck and were used as received. Freshly boiled, doubly distilled water was used throughout the synthetic procedures.

2.1. Physical Measurements. IR spectra were recorded on a Perkin-Elmer RXI FT-IR spectrophotometer in the range of 4000−600 cm^{-1} with the sample prepared as a KBr pellet. Elemental analyses (C, H, N) were performed on a Perkin-Elmer 240C elemental analyzer. TG experiments were carried out using a Mettler Toledo TGA/SDTA 851^e system.

2.2. Synthesis of $[TTPH_2](Cl)_2\cdot 4H_2O$ (1) and $[TTPH_2](Br)_2\cdot 4H_2O$ (2) (TTP = 4′-*p*-tolyl-2,2′:6′,2″-terpyridine, $C_{22}H_{17}N_3$). The TTP ligand was prepared following literature method.[16] Suspensions of TTP ligand (1.0 mM, 0.323 g) in water were reacted with HCl or HBr at room temperature (∼25.0 °C) with continuous stirring until the pH reached ∼1.0 and were then filtered to remove any undissolved materials. The yellow filtrate in either situation was kept for crystallization at room temperature. Needlelike yellow single crystals of **1** and needlelike reddish-yellow single crystals of **2** were separated after several days from the mother liquor by slow evaporation at room

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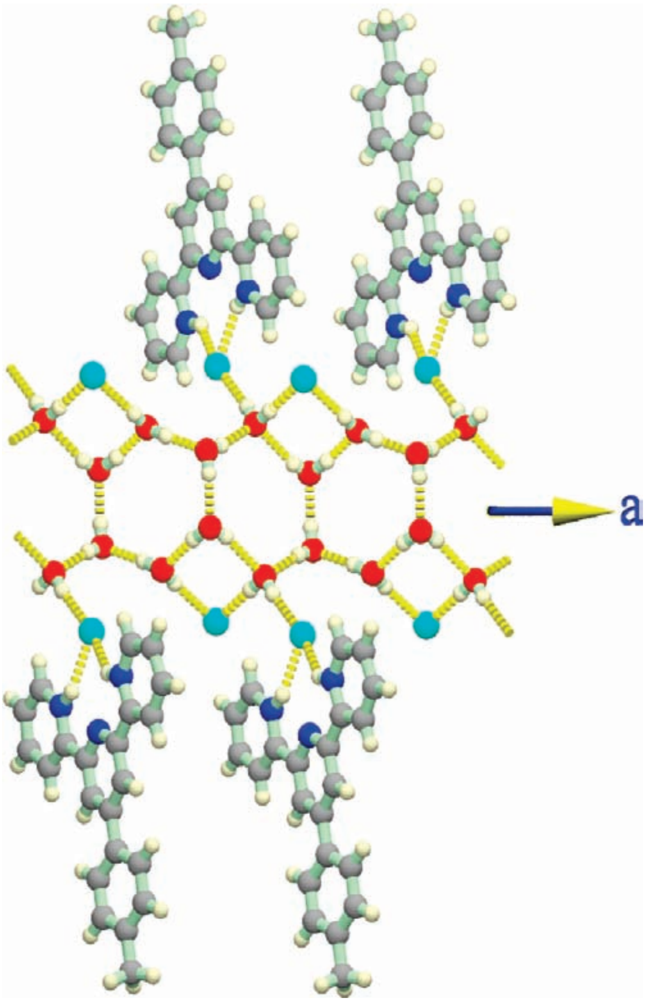

Figure 1. Supramolecular assembly of water−chloride tape in **1**. Arrow indicates the direction of propagation of water−chloride tape.

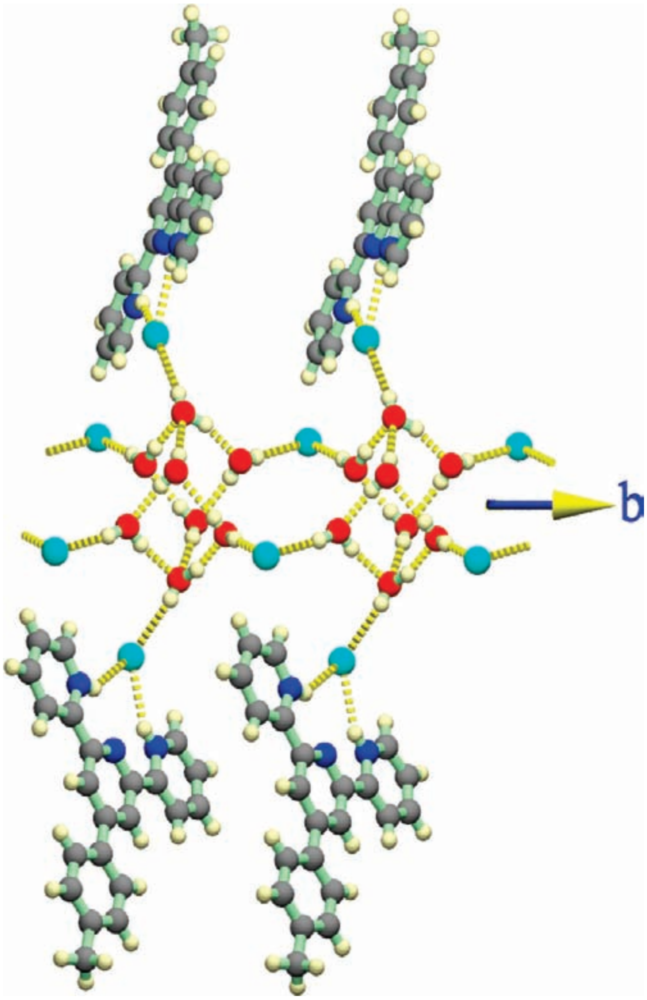

Figure 2. Supramolecular assembly of water−bromide chain in **2**. Arrow indicates the direction of propagation of water−bromide chain.

temperature. The crystals were separated by filtration, washed with ice-cold water, and then air dried. Anal. Calcd for $C_{22}H_{27}N_3O_4Cl_2$ (**1**): C, 56.36; H, 5.76; N, 8.96. Found: C, 56.24; H, 5.52; N, 8.77. Anal. Calcd for $C_{22}H_{27}N_3O_4Br_2$ (**2**): C, 47.37; H, 4.84; N, 7.53. Found: C, 47.22; H, 4.65; N, 7.41.

2.3. X-ray Crystal Structure Determination of 1 and 2. Crystals with suitable dimensions for **1** and **2** were mounted on a Bruker SMART APEX II diffractometer equipped with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 150(2) K. A total of 15 874 and 31 346 reflections were measured for **1** and **2**, respectively. A total of 5011 [$I > 2\sigma(I)$] and 4904 [$I > 2\sigma(I)$] data for **1** and **2**, respectively, were used for solution and refinement by full-matrix least-squares on F^2 with the SHELX-97 package.[17] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms. The final *R* values are 0.0308 and 0.0234 for **1** and **2**, respectively. CCDC nos. 697306 (for **1**) and 697307 (for **2**) contain the supplementary crystallographic data for this article.

2.4. Computational Details. All calculations were carried out using the Gaussian03 suite of programs.[18] To estimate the formation energies of models 1/X and 2/X (on the basis of the X-ray structures depicted in Figures 1 and 2, respectively, with the original anion replaced by $X = F^-, Cl^-, Br^-, I^-$), single-point calculations were carried out directly on the experimental structures employing the B3LYP[19,20] functional combined with Pople's[21a] basis sets 6-31+G(d,p) and the Lanl2DZ basis set on the iodine atom.[21b−d] The use of polarization (on both hydrogen and heavy atoms) and diffuse functions (s and p functions on heavy atoms) represents a good trade-off between computational cost and a reliable treatment of H-bond interactions.[22]

To quantify the intermolecular interactions in model 1/Cl(Br) and model 2/Cl(Br), the electron density was analyzed using the Bader's theory of atoms-in-molecules (AIM).[23,24] The AIM theory characterizes the interaction between atoms through critical points (where the gradient of the electron density ($\nabla\rho$) vanishes) and defines the connection path between two atoms. It has been demonstrated that the electron density (ρ) evaluated at specific critical points (named as bond critical points) correlates with the strength of bonding interactions such as covalent bonds, hydrogen bonding and π-stacking contacts.[25−28] As a reference for the reader: (i) the values of the electron density (calculated at the BHandH/6-311++G(d,p) level) in water, argon, and benzene dimers are 0.0343, 0.0059, and 0.0141 au, respectively,[28] and (ii) a variation of ~0.01 au calculated at the B3LYP/DGDZVP level for a diverse set of hydrogen-bonded systems roughly corresponds to a change of 2 kcal mol^{-1} in the interaction energy.[29]

To investigate the structural properties of the studied assemblies qualitatively, full geometry optimizations (with no constraints) were performed using both the AM1[30] and PM3[31] semiempirical Hamiltonians.[22a] Obtained geometries were then compared with the experimental structures (X-ray structures of **1** and **2**), focusing on the effect of the different anions on the resulting framework of water molecules. In particular, Figure S1 in the Supporting Information[32] shows the superimposed structure of **1** obtained from optimizations and from the X-ray experiments.

2.5. Reliability of Density Functional Theory and Semiempirical Calculations. DFT calculations have been widely applied to many areas of scientific interest, ranging from catalysis to DNA and drug−DNA structures.[33−45] Among many successful DFT functionals, B3LYP ensures a broad agreement with experimental results.[22a] However, the size of the systems (238 atoms for model 1 and 230 atoms for model 2[46]) prevented the geometry optimization at this level. Therefore, single-point calculations (and the AIM analysis) were carried out directly on the experimental X-ray structures, in line with previous studies that are fully or partially based on experimental structures, where molecular properties such as, for example, the electron density were calculated.[47−53]

Calculations based on AM1 and PM3 Hamiltonians may be less reliable (but less CPU demanding) than ab initio and DFT calculations. This is mainly due to the fact that some of the two-electron integrals employed for the construction of the Fock matrix (such as in Hartree−Fock methods, for instance) are replaced by parameters tuned on experimental values, high-level calculations, or both.[22a,54] Despite these approximations, semiempirical methods have been extensively and successfully employed for geometry optimizations and energy calculations of systems whose size would prevent the use of more quantitative calculations.[55−58] Indeed, a good qualitative agreement was achieved between the experimental and theoretical structures in the present investigation. The best results were obtained for compound **1** using PM3 (Figure S1 in the Supporting Information[32]).

3. Results and Discussion

3.1. Preliminary Observations. The chloride and bromide salts of a terpyridine derivative viz. $C_{22}H_{19}N_3 \cdot 4H_2O \cdot 2Cl$, designated as $[TTPH_2](Cl)_2 \cdot 4H_2O$ (**1**), and $C_{22}H_{19}N_3 \cdot 4H_2O \cdot 2Br$, designated as $[TTPH_2](Br)_2 \cdot 4H_2O$ (**2**), (TTP = 4′-*p*-tolyl-2,2′:6′,2″-terpyridine, $C_{22}H_{17}N_3$) have been prepared, where in both **1** and **2**, prominent O−H stretching frequencies were observed, respectively, at 3379 and 3385 cm^{-1}.[32] Results of IR and TG experiments, in detail, can be found in the Supporting Information (Figures S2−S7).[32]

3.2. Crystallographic Observations. Table S1 in the Supporting Information collects crystallographic data for **1** and **2**.[32] The asymmetric units of both **1** and **2** consist of one doubly protonated TTP molecule, four water molecules, and two chloride anions for **1**, whereas **2** consists of two bromide anions. Figure 3 represents the atom numbering scheme of the doubly protonated TTP molecule. The doubly protonated TTP molecule is planar, consisting of one phenyl ring and three pyridine rings. The N atoms (N1, N2, and N3) on the three adjacent pyridine rings generate an isosceles triangle with N1 at the tip of the central pyridine ring forming the apex of the triangle, and N2 and N3 form the base. Both protonated N2 and N3 atoms are involved in hydrogen bonding interactions with a common H acceptor (Cl2 in **1** and Br2 in **2**) as a result of the symmetric nature of the TTP molecule with respect to an axis that passes through the pyridine nitrogen atom N1 and the methyl carbon atom C1 (Figure 3). Therefore, the protonated TTP molecules act as receptor for chloride and bromide ions. Moreover, because of the availability of four aromatic rings, protonated TTP species organize themselves through π−π stacking interaction along a direction perpendicular to the plane of the molecule. Herein, these specific supramolecular features are utilized, leading to 2D arrays of self-organized $TTPH_2$ species, whose interlayer spaces are occupied by 1D water−anion networks. These packing features have been depicted in Figure 4 (for **1**), showing that the stacking of the $TTPH_2$ species in **1** is along the *a* axis. The water chloride chains are along the stacking direction (Figure 1).

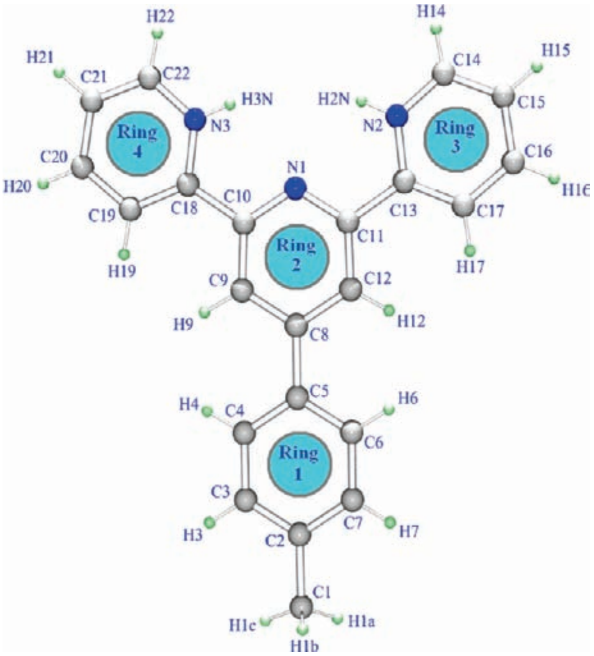

Figure 3. Doubly protonated TTP molecule in both **1** and **2** with atom numbering scheme. Rings have been marked as Ring 1, Ring 2, Ring 3, and Ring 4 for easy reference to the π−π interaction data that is presented in Table S2 in the Supporting Information.[32]

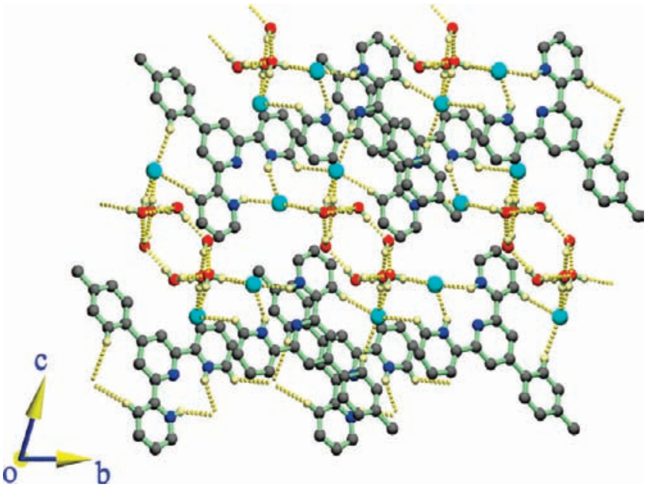

Figure 4. Packing diagram for complex **1** showing the position of water−chloride tapes in between the layers of π−π stacked doubly protonated TTP species.

In **1**, the chloride ions (Cl1 and Cl2) and the water molecules are perfectly fitted into the voids between the layers of π−π stacked $TTPH_2$ species (Figure 4) through a recognition process in which the $TTPH_2$ species act as receptor for both sets of chloride ions (Cl1 and Cl2) (Figure 5a). Whereas one set of chloride ions (Cl2 set of ions) is recognized through N−H···Cl hydrogen bonds (N2−H2N···Cl2 and N3−H3N···Cl2), the

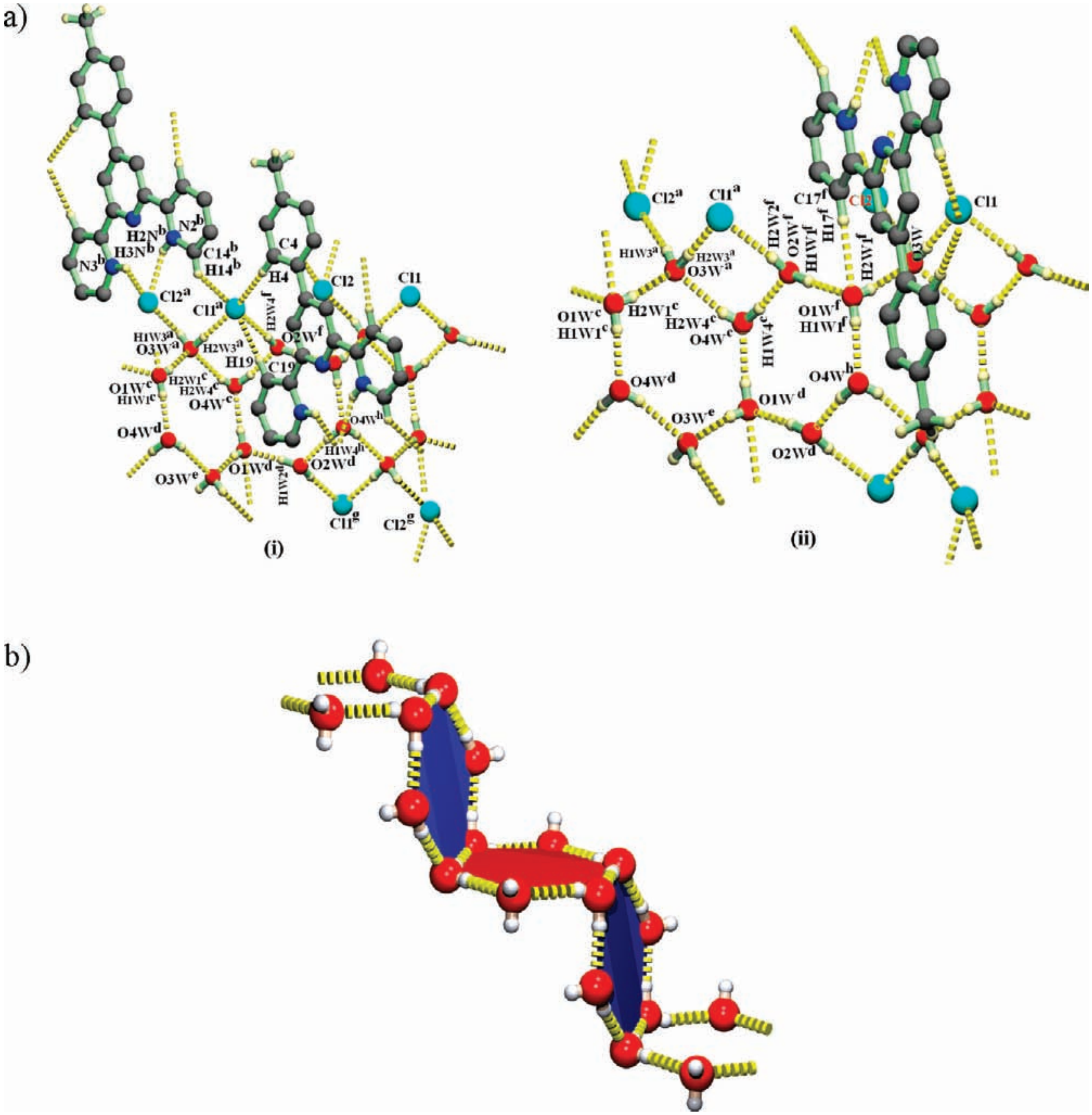

Figure 5. (a) Hydrogen bonds among water molecules, chloride anions, and the TTPH$_2$ species in **1**. (i) shows the C−H···Cl hydrogen bonds, whereas (ii) shows the C−H···O hydrogen bonds. Symmetry codes: $a = 1 + x, y, z$; $b = 1 + x, -1 + y, z$; $c = 2 - x, 1 - y, 1 - z$; $d = 1 + x, y, -1 + z$; $e = 2 - x, 1 - y, -z$; $f = 1 - x, 1 - y, 1 - z$; $g = 1 - x, 1 - y, -z$; $h = x, y, -1 + z$. (b) Staircase-like architecture of the water tape in **1**.

other set of chloride ions (Cl1 set of ions) is recognized by C−H···Cl hydrogen bonds (C4−H4···Cl1 and C19−H19···Cl1) (Figure 5a, Table 1).

The TTPH$_2$−chloride complexes are arranged on both sides of a unique water−chloride tape (Figure 1) through hydrogen bonding interactions. Four water molecules and one set of chloride ions (Cl1 set of ions) take part in this water−chloride assembly to generate a 1D tape. The core of this tape is constituted by planar water hexamers, and the tape is generated through fusion of successive water hexamers. The resulting tape has a staircase-like architecture (Figure 5b) with the adjacent water hexagons nearly perpendicular to each other (∼86°). The Cl1 set of ions position themselves at the two edges of this staircase (Figure 5a). Each of the chloride anions (Cl1 set) acts as common acceptor for two water molecules (O2W and O3W) at the tip of the adjacent steps and bridges them. These chloride ions (Cl1 set) act as a stabilizer for these unusual water tapes with staircase-like architecture, and this has been confirmed by theoretical calculations. (See the Theoretical Observations, vide infra). The other set of chloride ions (Cl2 set) that is recepted by the TTPH$_2$ species acts as an acceptor for one of the water molecules (O3W) on the water−chloride tape, satisfying its donor−acceptor balance. The details of the hydrogen-bonding arrangement for this water−chloride assembly and the TTPH$_2$ species in **1** is presented in Figure 5a, and the hydrogen-bonding parameters are listed in Table 1. The water hexamer is the basic building block of ice, I_h.[59] Hexameric water clusters have a number of stable structures that are nearly isoenergetic and which can adopt different conformations, that is, book, boat, cage, cyclic−planar, prism, and chair.[60] The boat and chair

TABLE 1: Hydrogen-Bonding Parameters in 1

D−H···A	D−H (Å)	H···A (Å)	D···A (Å)	<D−H−A (deg)	symmetry
O1W−H1W1···O4W	0.80(2)	1.94(2)	2.7349(16)	175(3)	$1 - x, 1 - y, 2 - z$
O1W−H2W1···O3W	0.772(19)	2.073(19)	2.8377(16)	171(2)	$1 - x, 1 - y, 1 - z$
O2W−H2W2···O1W	0.97(3)	1.84(3)	2.8018(17)	170(2)	
O4W−H2W4···O3W	0.71(2)	2.19(2)	2.8859(16)	164(2)	$1 - x, 1 - y, 1 - z$
O4W−H1W4···O2W	0.93(3)	1.84(3)	2.7622(16)	171(2)	$1 + x, y, z$
O2W−H1W2···Cl1	0.81(2)	2.33(2)	3.1370(11)	174(2)	$-x, 1 - y, 1 - z$
O3W−H2W3···Cl1	0.88(2)	2.23(2)	3.1014(11)	176(2)	
O3W−H1W3···Cl2	0.88(2)	2.34(2)	3.2058(11)	171(2)	
N2−H2N···Cl2	0.88	2.32	3.0932(9)	146.0	$x, 1 + y, z$
N3−H3N···Cl2	0.88	2.34	3.0979(10)	144	$x, 1 + y, z$
C4−H4···Cl1	0.95	2.81	3.7263(12)	163	$1 + x, y, z$
C14−H14···Cl1	0.95	2.74	3.4005(12)	128	$x, 1 + y, z$
C19−H19···Cl1	0.95	2.60	3.5406(12)	171	$1 + x, y, z$
C17−H17···O1W	0.95	2.39	3.3324(16)	170	

cyclohexamers have been found to be the basic building blocks of a number of polymeric water assemblies including a 1D tape[61] and 2D sheets[62] of water clusters. Hexameric water tapes have been found in two forms: vertex-shared[63] and edge-shared.[61a] Although edge-shared planar water tapes[61a] have been previously observed, to the best of our knowledge, the staircase-like architecture of planar water hexamers such as those found in **1** has not yet been reported.

As expected, the replacement of the chloride ions by bromide ions, applying identical reaction conditions, leads to the formation of a TTP-bromide complex, **2**, through a similar recognition mode. However, the presence of bromide ions influences the water assembly drastically, even though its basic 1D polymeric nature remains intact. In **2**, 3D discrete open-cube octameric units are observed instead of planar hexamers. These building units are doubly bridged to each other through two bromide ions forming a 1D chain of open-cube octamers (Figures 2 and 6). The hydrogen bonding between the water molecules, bromide anions, and $TTPH_2$ species is shown in Figure 6. The relevant hydrogen bonding parameters for **2** are given in Table 2. The open cube octamer found in **2** has nearly identical geometrical parameters with a similar motif reported once earlier.[64] In the present case, the octamers are bridged by bromide ions to generate a chain of water−bromide clusters, but the previously reported one[64] is a discrete open cube octamer. The packing diagram illustrating the disposition of these water−bromide chains in between the $\pi-\pi$ stacked layers of $TTPH_2$ species has been depicted in Figure 7. The $\pi-\pi$ interaction data for both **1** and **2** are tabulated in Table S2 of the Supporting Information.[32]

3.3. Theoretical Observations. A systematic theoretical investigation has been carried out on compounds **1** and **2** to evaluate the stability of the assemblies and the influence of the halide ions on the different spatial arrangements observed. Two models have been considered for this study, which have been defined as model 1/X (based on the X-ray structure of compound **1**; Figure 1) and model 2/X (based on the X-ray structure of compound **2**; Figure 2). Calculations have been carried out on these two models, replacing the original anion by all of the different halides, namely, with $X = F^-, Cl^-, Br^-, I^-$. Using this nomenclature scheme, models 1/Cl and 2/Br correspond to **1** and **2**, respectively. (See the Computational Details.)

First, full geometry optimizations (with no constraints) based on semiempirical methods were performed to examine the structural stability of the assemblies characterizing models 1/X and 2/X. These calculations show that upon optimization, the structure of model 1/Cl hardly changes, with the H-bonding interactions of the staircase water cluster being substantially

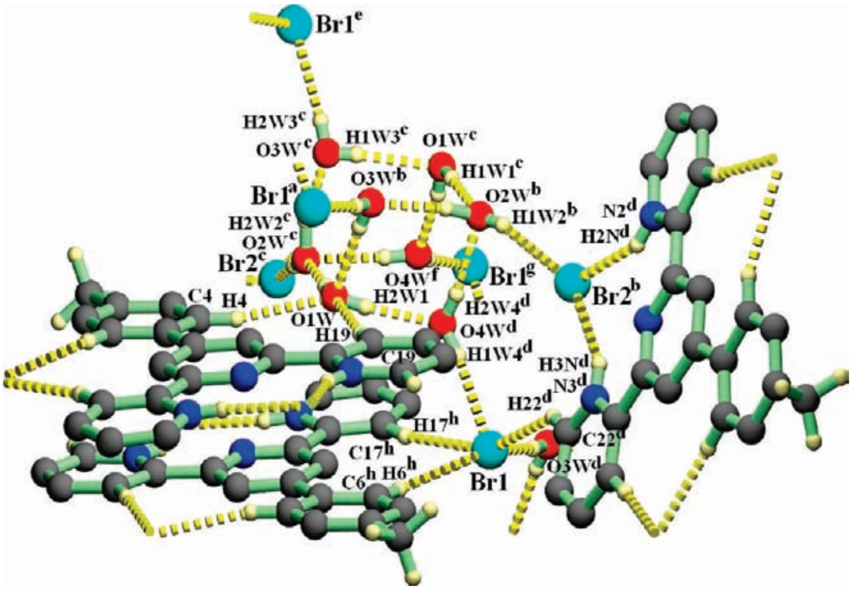

Figure 6. Hydrogen bonds among water molecules, bromide anions, and the $TTPH_2$ species in **2**. Symmetry codes: $a = x, 1 + y, z$; $b = {}^1/_2 - x, {}^1/_2 + y, {}^1/_2 - z$; $c = {}^1/_2 + x, {}^1/_2 + y, z$; $d = {}^1/_2 - x, -{}^1/_2 + y, {}^1/_2 - z$; $e = 1 - x, 1 + y, {}^1/_2 - z$; $f = {}^1/_2 - x, -{}^1/_2 + y, {}^1/_2 - z$; $g = 1 - x, y, {}^1/_2 - z$; $h = {}^1/_2 - x, 3/2 - y, -z$.

TABLE 2: Hydrogen-Bonding Parameters in 2

D−H···A	D−H (Å)	H···A (Å)	D···A (Å)	<D−H−A (deg)	symmetry
O1W−H1W1···O2W	0.75(4)	2.13(4)	2.886(3)	176(3)	$\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$
O1W−H2W1···O4W	0.79(3)	1.95(3)	2.733(2)	172(3)	$x, -1 + y, z$
O2W−H2W2···O3W	0.93	1.86	2.760(2)	161	
O3W−H1W3···O1W	0.73(3)	2.13(3)	2.855(2)	175(3)	$\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$
O4W−H2W4···O2W	0.83	2.00	2.821(2)	170	$-\frac{1}{2} + x, 3/2 - y, -\frac{1}{2} + z$
O2W−H1W2···Br2	0.76(3)	2.68(3)	3.4274(19)	166(3)	$\frac{1}{2} + x, \frac{1}{2} + y, z$
O3W−H2W3···Br1	0.82(4)	2.47(3)	3.289(2)	175(3)	$1 - x, -y, 1 - z$
O4W−H1W4···Br1	0.90	2.40	3.2863(19)	171	$\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$
N2−H2N···Br2	0.84(2)	2.53(3)	3.2664(16)	148(3)	$\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$
N3−H3N···Br2	0.84(3)	2.54(3)	3.2687(19)	146(2)	$\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$
C4−H4···O1W	0.95	2.48	3.409(2)	166	
C19−H19···O1W	0.95	2.58	3.528(3)	174	
C6−H6···Br1	0.95	2.88	3.7827(18)	160	$x, 1 - y, \frac{1}{2} + z$
C17−H17···Br1	0.95	2.84	3.769(2)	166	$x, 1 - y, \frac{1}{2} + z$
C22−H22···Br1	0.95	2.77	3.548(2)	139	

preserved. Interestingly, replacement of Cl^- by Br^- hardly affects the overall structure. Similarly, the water cluster geometry is fully conserved during optimization of model 2/Br (with a slight rearrangement of $TTPH_2$ species, Figure S8 in the Supporting Information[32]). Replacement of Br^- by Cl^- results in drastic changes, with the modification of the water clusters as well. In addition, our calculations confirm the intuitive idea that the anions are crucial for the stability of the entire assembly. Indeed, complete removal of the anions strongly affects the structures of both models, with significant alterations in model 2. In this particular case, the $TTPH_2$ species rearrange around the water molecules to minimize the electrostatic repulsion (Figure S9 in the Supporting Information[32]). Despite the limitations inherent to semiempirical approaches (Computational Details), the results achieved here show that the water clusters obtained experimentally are substantially stable upon full optimization.

Second, B3LYP/6-31+G(d,p) single-point calculations were carried out directly on the experimental structures (i.e., derived from the X-ray structures of **1** and **2**, replacing the original anion with X = F^-, Cl^-, Br^-, and I^-, Table 3) to estimate the formation energies (ΔE in kilocalories per mole). In the first instance, these calculations confirm the qualitative data obtained by using semiempirical methods: the removal of the anions leads to a substantial instability of the supramolecular assemblies (Table 3). Most importantly, single-point calculations suggest that the nature of the anion may be crucial for the stability of the final self-assembly, as shown by the solid-state structures (Figures 1 and 2). For instance, a relationship between the formation energy and the nature of the anion is noticed; for example, the assemblies with F^- are more stable than those with I^-. Remarkably, the present computational results are in agreement with previous experimental and more refined theoretical studies dealing with the stability of smaller halide-water, hydrogen-bonded clusters, where the formation energy of the supramolecular aggregates containing more than three to four water molecules follows the same trend as that in Table 3, that is, $F^- > Br^- > Cl^- > I^-$.[58a,b]

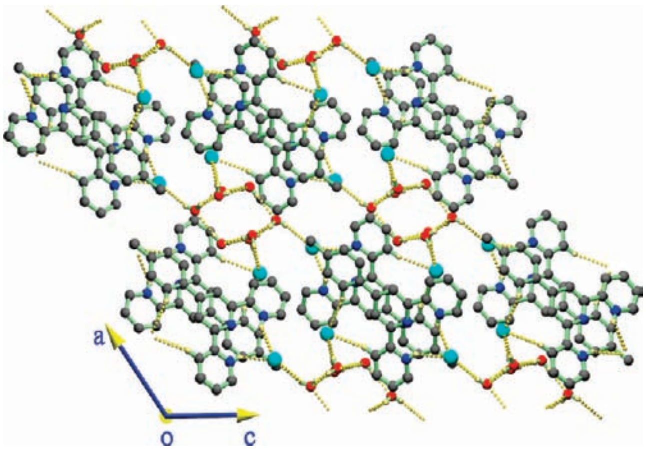

Figure 7. Packing diagram for complex **2** showing the position of water−bromide chains in between the layers of $\pi-\pi$ stacked doubly protonated TTP species.

TABLE 3: Formation Energies (ΔE, kilocalories per mole) of Models 1/X and 2/X (with X = F^-, Cl^-, Br^-, I^-) Calculated via Single-Point Calculations at the B3LYP/6-31+G(d,p) Level on the X-ray Structures of Compounds 1 and 2 (with the Original Anion Replaced by X = F^-, Cl^-, Br^-, or I^- Anion)[a]

formation energy (ΔE)	X = none	X = F^-	X = Cl^-	X = Br^-	X = I^-
model 1	+520	−312	−247[b]	−265	−105
model 2	+780	−522	−340	−459[b]	−298

[a] It has to be stressed that the energies of model 1 cannot be directly compared with those of model 2 because these assemblies have a different number of atoms. [b] Ion in the original crystal structure from Figures 1 (model 1) and 2 (model 2).

These data also suggest that both assemblies may be more thermodynamically stable when Br^- ions are employed; for example, the formation energies of models 1/Br and 2/Br are larger than those of models 1/Cl and 2/Cl. Therefore, the fact that the structure of model 1 is observed experimentally only when Cl^- is employed suggests that factors besides thermodynamics may play a role, such as kinetics, anion diffusion (which may depend on the size of the anions;[65] that is, 0.172 nm for Cl^- and 0.196 nm for Br^-, and the calculated interaction energies for aqueous ionic clusters, ΔE_{int}, in $Cl(H_2O)^-$ and in $Br(H_2O)^-$ clusters, which are −14.6 for $Cl^- \cdots H_2O$ and −12.9 kcal mol^{-1} for $Br^- \cdots H_2O$), or both.[66] The investigation of these subtle phenomena requires higher-level calculations (for instance, DFT coupled to larger basis sets) and more realistic models of the crystal. However, the size of the studied systems (about 230 atoms) makes this a nontrivial task beyond the capacity of our computational resource.

To better describe the intermolecular interactions that characterize these assemblies, the AIM analysis has been carried out. It has to be noted that the electron density evaluated at the bond critical points has been shown to correlate with the strength of bonding interactions, including H bonds. (See the Computational Details.)

TABLE 4: Average Values of the Electron Density (ρ, au) at the Bond Critical Points of the Hydrogen Bonds between Water Molecules, TTP, and Anions in Models 1/X and 2/X ($X = Cl^-, Br^-$)[a]

model	(water)O−H···O (water)	(water) O−H···X	(TTP) N−H···X
1/Cl	0.0240	0.0183	0.0260
1/Br	0.0241	0.0211	0.0390
2/Br	0.0210	0.0128	0.0227
2/Cl	0.0210	0.0119	0.0170

[a] Values are obtained via single-point calculations at the B3LYP/6-31+G(d,p) level.

First, the AIM analysis has been used to monitor the effect of changing the anion within the same model. This approach indicates that the hydrogen-bonding strength between water molecules, that is, (water)O−H···O(water), is hardly affected by the nature of the anions (e.g., the electron density is hardly modified, Table 4). In contrast, the interactions of the anions with protonated TTP species and with water molecules, namely, (TTP)N−H···X and (water)O−H···X, do depend on the nature of the anion itself. For instance, for model 1, the electron density at the bond critical point of (TTP)N−H···Br is significantly larger than that of (TTP)N−H···Cl, with $\rho = 0.0390$ versus 0.0260 au on average (Table 4); the (water)O−H···Br interactions are slightly stronger than the (water)O−H···Cl ones, with $\rho = 0.0211$ and 0.0183 au. Similar trends are observed for model 2 (Table 4).

Second, the AIM analysis provides hints about the relative strength of the intermolecular interactions characterizing models 1 and 2 (Table 4). In particular, all hydrogen bonds are stronger in model 1/Cl (compound **1**) as compared with those of model 2/Br (compound **2**). For instance, the average electron density of the water···water interaction, that is, (water)O−H···O(water), is 0.0240 for **1** and 0.0210 au for **2**. Similarly, the average electron densities of (water)O−H···X and (TTP)N−H···X are 0.0183 (**1**) and 0.0128 (**2**) au and 0.0260 (**1**) and 0.0227 (**2**) au, respectively. This may represent a key issue justifying the structural stability of **1** observed during the semiempirical optimization.

4. Concluding Remarks

In summary, we report here water−chloride and water−bromide clusters that are extensively characterized by experimental and theoretical techniques. The main outcome of this study is the observation of new and interesting water−halide assembly, showing a 1D water−chloride tape with staircase-like architecture of planar water hexamers and a 1D polymeric chain of discrete open-cube octameric units of water bridged by bromide anions.

The crystal structures of the water−chloride and water−bromide assembly reported here reveal that the doubly protonated TTP molecules, viz. $[TTPH_2]^{2+}$ species, can act as appropriate receptors for halide ions, which in turn act as a matrix for the formation of polymeric 1D water/halide assemblies. The water−anion assemblies herein reported have been theoretically investigated.

Despite their qualitative character, the semiempirical calculations carried out in the present study suggest that the structures of the water clusters obtained experimentally are fairly stable upon full optimization and (as expected) fall apart when the anions are removed. Moreover, B3LYP/6-31+G(d,p) single-point calculations, in line with semiempirical optimizations, show that the nature of the anion may affect the specific features of the assemblies studied. Indeed, the AIM analysis indicates that the original staircase-like water cluster of **1** (model 1) is characterized by a stronger hydrogen bonding pattern than that of **2** (model 2). In addition, electron density analysis suggests that the water···water hydrogen bonding interactions are virtually independent of the anion employed in both models 1 and 2. However, the (TTP)N−H···X and (water)O−H···X hydrogen bonds do depend on the nature of the anion: those involving Br^- are stronger than those with Cl^-.

On the basis of the data reported herein, it is believed that the fact that the nature of the anion used leads to different solid-state structures is partially due to the possibility of tuning the strength of the (water)O−H···X and the (TTP)N−H···X hydrogen bonds. In addition, one should also consider the factors such as kinetics and anion diffusion (which is linked to the size of the anions) that likely play an important role in the formation of these supramolecular assemblies.

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Supporting Information Available: AM1- and PM3-optimized structures of models 1/Cl and 1/Br, TG curves of complexes **1** and **2**, FTIR spectra of complexes **1** and **2**, PM3-optimization of models 2/Br (compound **2**) and 2/Cl, rearrangement of the molecules in **2** when the anions are removed, crystallographic data of complexes **1** and **2**, and $\pi-\pi$ interaction data in **1** and **2**. Full crystallographic data in CIF format for **1** and **2** have been deposited with the Cambridge Crystallographic Data Centre (CCDC 697306 for **1** and 697307 for **2**). Copies of these data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, U.K.; Fax: +44(0)-1223-336033; E-mail: deposit@ccdc.cam.ac.uk. This material is available free of charge via the Internet at http://pubs.acs.org.

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