Novel sheet-like supramolecular architectures constructed from infinite hydrogen-bonded, protonated adenine–water–halide and polyiodide ribbons

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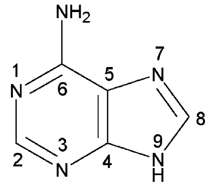
A series of novel supramolecular architectures are constructed from self-assembly of adenine (Ade), hydrogen halide and polyiodides. They are $[AdeH_2^{2+}](X^-)(I_5^-)(H_2O)$ [**1**, X = Cl; **2**, X = Br] and $[AdeH_2^{2+}](I_6^{2-})(H_2O)_2$ (**3**). All three architectures are sheet-like nanosized structures made up of alternately arranged positive and negative ribbons of *ca.* 1 nm width. The positive ribbon is built by halide anions or iodide–water pair bridged $(AdeH_2^{2+})_2$ dimers with extra water acceptors through hydrogen bonds, and the negative ribbon is constructed from twinned zigzag polyiodide chains. Both ribbons are zigzag shaped and have good complementarity in the shape, size, charge and inter-ribbon interactions in the architectures.

The self-assembly of nanosized structures from small molecular units or the so-called "bottom-up" methodology is of continuous interest because of its potential use to construct molecular devices.[1] Polyiodides and nucleobases are two classes of chemical species for this purpose. Polyiodides could serve as charge acceptors in many charge transfer complexes with interesting electrical behavior[2] or show some interesting electrical properties themselves.[3] Studies on polyiodides in many types of supramolecular architectures manifest several unique characteristics of the polyiodide species. They show a wide structural diversity, from various discrete oligomeric anions to numerous extended 1D, 2D and 3D networks, due to the varied strengths and the flat potential energy surfaces of I···I interactions.[4] The formation and topology of polyiodide species depend on the characteristics, such as shape, size and charge, *etc.*, of the counter cations, which therefore are usually considered as templating agents.[5] Rich, complicated and fascinating intermolecular interaction patterns such as hydrogen bonds (both conventional and weak), π–π interactions and embraces and the complementarity between cations and polyiodide anions have been observed. On the other hand, nucleobases or their derivatives, being neutral or protonated, possess multiple hydrogen-bonding sites and various tautomers so that they can form an abundance of aggregates through hydrogen bonds, from the famous Watson–Crick pairs to infinite extended structures.[6] This property has been applied to design and construct highly ordered hydrogen-bonded supramolecular linear nanostructures in both 3D crystals and 2D surfaces, which may act as proton or electron nanowires.[7] They are planar and aromatic, and therefore they would be suitable for intermolecular stacking and π–π interactions. In particular, they may have complementarity with polyiodide species, like other aromatic nitrogen bases and arylated cations. Therefore, it should be expected that protonated nucleobases could act as an interesting and unique class of templates, especially as hydrogen-bonded extended templates, to construct novel nanosized assemblies with polyiodides.

Combination of protonated adenine and cytosine with polyiodides led to the first two supramolecular architectures, assembled by unique hydrogen-bonded nucleobase–water ribbons and unusual polyiodide species.[8] Both of them are nanosized supramolecular structures and display fascinating interactions and good complementarity between the two counter-charged parts. In this work, we report the synthesis and structures of three novel supramolecular architectures, $[AdeH_2^{2+}](X^-)(I_5^-)(H_2O)$ [**1**, X = Cl; **2**, X = Br] and $[AdeH_2^{2+}](I_6^{2-})(H_2O)_2$ (**3**), where Ade is adenine. They are all sheet-like structures constructed from alternately arranged positive and negative ribbons of nanometer width. The positive ribbon is made up of hydrogen-bonded bi-protonated adenines, water and halide anions, while the negative ribbon is built up by unusual twinned zigzag polyiodide chains.



Adenine

Experimental

Synthesis

All chemicals were used as received without further purification.

1. Adenine (0.064 g, 0.47 mmol), KI (0.271 g, 1.63 mmol) and I_2 (0.202 g, 0.80 mmol) were added to a mixed solution of 7 ml ethanol, 3 ml water and 0.5 ml concentrated hydrochloric acid (36–38%). The solution was heated for about 5 min. The reagents were all dissolved and then the solution was filtered.

Orange-red plate-like crystals (271 mg) were obtained by slow evaporation of the solvent at room temperature for several weeks. Elem. anal. (%): found C 7.33, H 0.94, N 8.75: calcd C 7.28, H 1.10, N 8.49. The product was soluble in DMF, methanol, THF, acetonitrile and insoluble in chloroform, cyclohexane, and *n*-heptane. IR (cm^{-1}, peaks of strong absorption only): 3252, 3089, 1686, 1615, 1505, 1380, 911, 891, 715, 602, 539, 243, 181, 144.

2. Adenine (0.135 g, 1.00 mmol), KI (0.358 g, 2.16 mmol) and I_2 (0.512 g, 2.02 mmol) were added to a mixed solution of 15 ml ethanol, 4 ml water and 1.8 ml concentrated hydrobromic acid, (about 40%; **CAUTION**: hydrobromic acid is corrosive for skin and should be handled carefully). The solution was heated for about 5 min and then filtered. Red-brown block crystals (220 mg) were obtained by slow evaporation of the solvent at room temperature for several weeks. Elem. anal. (%): found C 7.16, H 1.13, N 7.88: calcd C 7.16, H 1.17, N 7.88. The product was soluble in DMF, methanol, THF, acetonitrile and insoluble in chloroform, cyclohexane, and *n*-heptane. IR (cm^{-1}, peaks of strong absorption only): 3089, 1688, 1614, 1446, 1395, 911, 891, 715, 619, 600, 556, 391, 164, 139.

3. Adenine (0.0649 g, 0.48 mmol), KI (0.1980 g, 1.19 mmol) and I_2 (0.2889 g, 1.14 mmol) were added to a mixed solution of 20 ml water and 1 ml concentrated hydrochloric acid (36–38%), yielding green deposits. The solution was filtered. Minor red-brown block crystals of **3** and a large amount of slightly yellow column crystals were obtained by slow evaporation of the solvent at room temperature for several weeks. The crystals of **3** (16 mg) were separated mechanically. Elem. anal. (%): found C 8.07, H 1.98, N 9.09: calcd C 6.42, H 1.19, N 7.49. The product was soluble in DMF, methanol, THF, acetonitrile and insoluble in chloroform, cyclohexane, and *n*-heptane. IR (cm^{-1}, peaks of strong absorption only): 3309, 3089, 1694, 1614, 1505, 1442, 1396, 1232, 1210, 910, 893, 715.

X-Ray crystallography

Intensity data for the three compounds were collected on a Nonius Kappa CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Cell parameters were obtained by the global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELX-97 package.[9] All non-hydrogen atoms were refined anisotropically. Locations of H atoms attached to O and N were justified by difference Fourier synthesis. The H atoms of water, located from the difference Fourier synthesis, were refined using the ideal geometry of free water molecules, in which the O–H bond lengths were constrained at 0.96 Å and the H–O–H angle at 104.5°, as well as the same freely refined isotropic thermal factors: 0.08(2) $Å^2$ in **1**, 0.09(2) $Å^2$ in **2**, and 0.13(2) $Å^2$ in **3**. H atoms attached to C and N were added geometrically and refined using the riding model. Details of crystallographic data for the structures are summarized in Table 1. Hydrogen bonds, both conventional and weak, are listed in Table 2 for **1** and **2** and in Table 3 for **3**.

CCDC reference numbers 186872–186874. See http://www.rsc.org/suppdata/nj/b2/b204805a/ for crystallographic files in .cif format.

Table 1 Crystallographic data for **1**, **2** and **3**

Compound	1	2	3
Formula	$C_5H_9ClI_5N_5O$	$C_5H_9BrI_5N_5O$	$C_5H_{11}I_6N_5O_2$
FW	825.12	869.58	934.59
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a/Å	8.2477(2)	8.4401(3)	12.4041(4)
b/Å	10.7053(3)	10.5059(4)	12.8322(5)
c/Å	10.4233(3)	10.6470(3)	12.5015(3)
α/°	103.0848(11)	102.676(2)	90
β/°	91.7871(15)	92.067(2)	105.352(2)
γ/°	100.8063(11)	101.7656(16)	90
U/$Å^3$	877.91(4)	898.48(5)	1918.88(11)
Z	2	2	4
T/K	293	293	293
μ (Mo Kα)/mm^{-1}	9.004	10.872	9.716
Total reflections collected	27746	17224	32992
Unique reflections	3987	4245	4564
R_{int}	0.0686	0.0494	0.0583
Observed reflections [$I \geqslant 2\sigma(I)$]	2778	3104	3402
R_1 [$I \geqslant 2\sigma(I)$]	0.0319	0.0396	0.0319
wR_2 [$I \geqslant 2\sigma(I)$]	0.0653	0.0938	0.0623
R_1(all data)	0.0605	0.0608	0.0537
wR_2 (all data)	0.0729	0.1036	0.0687

Results and discussion

Crystal structures of $[AdeH_2^{2+}](X^-)(I_5^-)(H_2O)$ [1, X = Cl; 2, X = Br]

1 and **2** are isomorphous, so the structure of **1** is mainly described here. In the structure all adenine molecules are bi-protonated to yield $AdeH_2^{2+}$ cations. Protonation occurs at the N1, N7 and N9 sites (Fig. 1), while the N3 site remains unprotonated. The protonation status of the N sites is also confirmed by the larger internal ring C–N–C angle at N1 (124.4°) than N3 (111.6°), and at N7 (108.0°) and N9 (107.8°) than reported values (*ca.* 103°) for the neutral N sites of the five-membered ring of adenine.[6] Two neighboring $AdeH_2^{2+}$ cations form a dimer through one pair of N9–H···N3 hydrogen bonds in a $R_2^2(8)$ pattern,[10] which is a

Table 2 Hydrogen bonding geometry in **1** and **2**[a]

D–H···A[b]	d(D–H)/Å	d(H···A)/Å	d(D···A)/Å	∠(DHA)/°
1				
N9–H5···$N3^{\#1}$	0.86	2.02	2.858(5)	164.8
N7–H3···O1	0.86	1.85	2.655(5)	154.0
N1–H1···$Cl1^{\#2}$	0.86	2.17	2.999(4)	161.5
N6–H6···$Cl1^{\#2}$	0.86	2.71	3.417(5)	140.0
N6–H7···O1	0.86	2.19	2.994(6)	156.1
C8–H4···Cl1	0.93	2.67	3.384(5)	133.8
$C2^{\#1}$–$H2^{\#1}$···Cl1	0.93	2.71	3.532(5)	147.5
O1–H9···I4	0.94(2)	3.23(5)	3.706(3)	114(4)
O1–H9···I2	0.94(2)	3.29(4)	3.959(4)	130(4)
C8–H4···I1	0.93	3.09	3.811(5)	135.2
O1–H8···$Cl1^{\#3}$	0.93(2)	2.20(2)	3.128(4)	175(5)
O1–H9···$I1^{\#4}$	0.94(2)	3.14(3)	3.899(4)	140(4)
2				
N9–H5···$N3^{\#1}$	0.86	2.02	2.859(6)	164.4
N7–H3···O1	0.86	1.87	2.668(6)	153.5
N1–H1···$Br1^{\#2}$	0.86	2.33	3.154(4)	160.9
N6–H6···$Br1^{\#2}$	0.86	2.77	3.502(5)	143.3
N6–H7···O1	0.86	2.16	2.966(7)	156.4
C8–H4···Br1	0.93	2.77	3.486(6)	134.4
$C2^{\#1}$–$H2^{\#1}$···Br1	0.93	2.83	3.650(6)	147.9
O1–H9···I4	0.94(2)	3.26(7)	3.695(4)	111(5)
O1–H9···I2	0.93(2)	3.35(6)	3.883(5)	119(5)
C8–H4···I1	0.93	3.07	3.775(6)	134.4
O1–H8···$Br1^{\#3}$	0.94(2)	2.42(4)	3.255(5)	147(6)
O1–H9···$I1^{\#4}$	0.93(2)	2.96(3)	3.822(5)	155(6)

[a] Note: Hydrogen bonds with symmetry transformations #3 and #4 are inter-sheet hydrogen bonds, the others are intra-sheet hydrogen bonds. [b] Symmetry transformations used to generate equivalent atoms: #1: $-x, -y+2, -z+1$; #2: $x, y, z-1$; #3: $-x, -y+1, -z+1$; #4: $-x+1, -y+1, -z+1$.

Table 3 Hydrogen bonding geometry in **3**^{a}

D–H···A^b	d(D–H)/Å	d(H···A)/Å	d(D···A)/Å	∠(DHA)/°
N9–H5···N3$^{\#1}$	0.86	2.11	2.944(5)	164.3
N6–H7···O1	0.86	2.04	2.859(6)	160.0
N7–H3···O1	0.86	1.98	2.754(5)	149.8
N1–H1···O2	0.86	2.05	2.843(6)	153.0
N6–H6···O2	0.86	2.33	3.050(6)	141.6
O2–H11···I6	0.94(2)	2.64(3)	3.554(4)	163(6)
C8–H4···I6$^{\#2}$	0.93	2.94	3.686(5)	138.1
C2–H2···I6$^{\#3}$	0.93	3.10	3.925(5)	148.5
C8–H4···I1	0.93	3.19	3.773(5)	122.5
O1–H9···I2	0.96(2)	2.99(6)	3.645(4)	127(5)
O1–H9···I4	0.96(2)	3.04(6)	3.738(4)	131(5)
O2–H10···I4$^{\#4}$	0.95(2)	2.98(5)	3.770(4)	142(5)
O2–H10···I3$^{\#4}$	0.95(2)	3.30(6)	3.999(4)	133(6)
O1–H8···I6$^{\#4}$	0.95(2)	3.15(3)	4.052(4)	159(5)
O1–H8···I5$^{\#4}$	0.95(2)	3.25(7)	3.826(4)	121(5)
O2–H10···I2$^{\#5}$	0.95(2)	3.32(5)	3.846(4)	118(4)

^{a} Note: Hydrogen bonds with symmetry transformations #4 and #5 are inter-sheet hydrogen bonds, the others are intra-sheet hydrogen bonds. ^{b} Symmetry transformations used to generate equivalent atoms: #1: $-x+1, -y, -z+1$; #2: $x, y-1, z$; #3: $-x+1, -y+1, -z+1$; #4: $-x, -y+1, -z+1$; #5: $x+1/2, -y+1/2, z-1/2$.

usual base-pairing mode, found for adenine and its derivatives.[6a,6b] The other peripheral hydrogen bond donors, C–H and N–H, of the dimer further form a series of N–H···O, N–H···Cl, C–H···Cl hydrogen bonds (Table 2) with the surrounding acceptors of two water molecules and four Cl$^-$ anions, yielding several hydrogen bonding patterns of ring type [Fig. 1(a)]. These motifs form a 1D zigzag shaped, positive ribbon of $[(\mathrm{AdeH_2}^{2+})_2(\mathrm{H_2O})_2(\mathrm{Cl}^-)_2]_n$, by sharing two Cl$^-$ anions between two neighboring dimers *via* N–H···Cl, C–H···Cl hydrogen bonds. In the ribbon, each Cl$^-$ anion accepts two N–H and two C–H donors, and it is 0.49 Å above or below the mean plane of the ribbon. The negative ribbon is two zigzag polyiodide chains twinned together [Fig. 1(b)], made up of nearly linear and symmetric I_3^- (I1–I2–I3) and I_2 (I4–I5) moieties. The zigzag chains of linked I_3^- and I_2 units are typical and long-known polyiodide species,[5,11] while the twinned zigzag chains have rarely been characterized before. The I–I distances can be divided into three categories: 2.756 Å in the I_2 unit and 2.872, 2.988 Å in I_3^-; 3.378 and 3.423 Å between the adjacent I_3^- and I_2 units in one chain, indicating quite strong $I_3^-\cdots I_2$ bonding; and 4.10 to 4.23 Å between the two twinned zigzag chains, showing weak inter-chain I···I interactions. These values are comparable with those found in other compounds.[5,8,11] Both of the ribbons run along the *c* direction in the lattice.

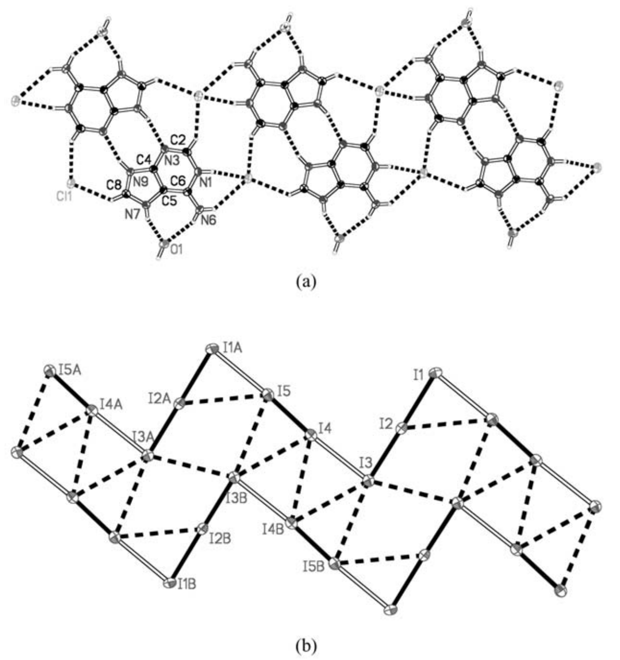


Fig. 1 (*a*) Ortep drawing of the positive ribbon composed by the dimer $(\mathrm{AdeH_2})_2^{4+}$, chloride ions and water molecules through hydrogen bonds (dashed solid bonds) in **1**. Hydrogen bonds between the two bi-protonated adenine cations in the dimer are: N–H···N 2.858 Å [2.859 Å in **2**]. (*b*) The twinned, zigzag shaped polyiodide ribbon in **1**, with atomic labeling scheme. The I–I bonds of I_2 and I_3^- moieties are highlighted by solid bonds. Dashed solid bonds indicate I···I interactions with I–I distances close to 4.2 Å. Symmetry codes: A: *x*, *y*, *z* −1; B: −*x* + 1, −*y*, −*z*.

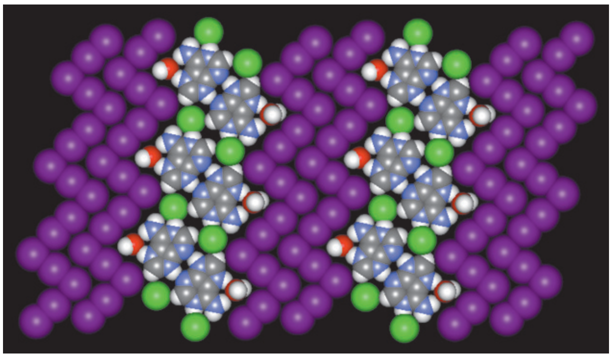


Fig. 2 One sheet composed of alternately arranged negative and positive ribbons in **1**. Color scheme: I purple, Cl green; O red; N blue; C gray; H white.

The positive and negative ribbons are all zigzag shaped, and of almost the same width, *ca.* 1 nm. They are complementary to each other in size, shape and charge. Thus, they form sheet-like structures in which the positive and negative ribbons are alternately arranged, and the zigzag sides of the neighboring ribbons are interlocked (Fig. 2). Numerous weak O–H···I and C–H···I hydrogen bonds between the counter-charged ribbons interweave them. These hydrogen-bond distances are 3.71–3.96 and 3.81 Å for O···I and C···I, respectively. The sheet is of good planarity except for the slight deviation off the sheet plane of the Cl$^-$ anions. In the lattice, these sheets stack along the *a* direction to form a 3D architecture through hydrogen bonding and electrostatic interactions between the counter-charged ribbons. The inter-sheet separation is *ca.* 3.6 Å. The positive ribbon in one sheet is clamped by two polyiodide ribbons of the adjacent two sheets, so that each positive ribbon is surrounded by four negative polyiodide ribbons, and *vice versa*. In the 3D architecture, the remaining O–H donors of water molecules form O–H···Cl and O–H···I type hydrogen bonds between the sheets, with O···Cl distances of 3.13 Å, and O···I ones of 3.90 Å. These hydrogen bonds make a slight overlap between the polyiodide ribbons of neighboring sheets, producing shorter intersheet I···I distances of 4.24 Å. All these weak interactions give extra stabilization to the architecture.

Crystal structure of $[\mathrm{AdeH_2}^{2+}](\mathrm{I_6}^{2-})(\mathrm{H_2O})_2$ (3)

3 also contains hydrogen-bonded $(\mathrm{AdeH_2}^{2+})_2$ dimers (Fig. 3) similar to those in **1** and **2**, but the dimer is now surrounded by four water molecules and two iodine anions, which belong to the polyiodide ribbons described later. These peripheral acceptors form quite similar hydrogen bonding (Table 3) patterns with the dimer to those in **1** and **2**. However, in this case the adjacent dimers share two $\mathrm{I}^-\cdots\mathrm{H_2O}$ hydrogen-bonded

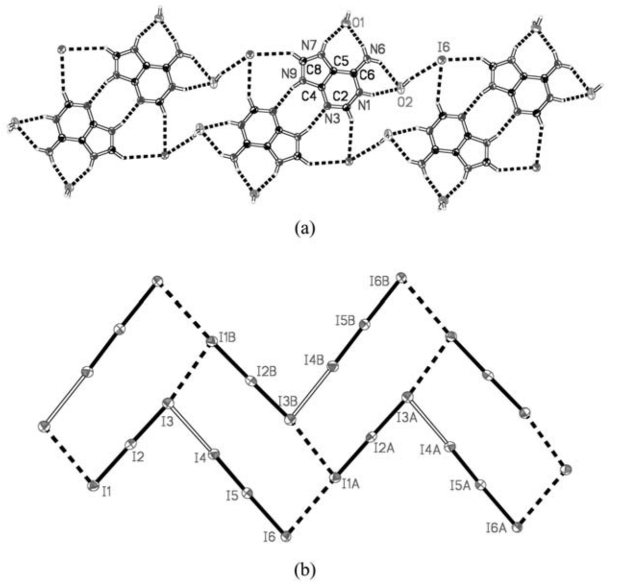


Fig. 3 (*a*) Ortep plot of the positive ribbon in **3**, built by dimers $(AdeH_2)_2^{4+}$, iodide ions and water molecules, with atomic labels and hydrogen bonds (dashed solid bonds). Within the dimer the hydrogen bonds between the two bi-protonated adenine cations are: N–H···N 2.944 Å. (*b*) The negative, twinned, zigzag shaped polyiodide ribbon composed of I_6^{2-} anions in **3**. Solid bonds highlight the I_3^- moieties and dashed solid bonds indicate weak I–I interactions. Symmetry code: A: *x*, *y* + 1, *z*; B: −*x* −0.5, *y* + 0.5, −*z* + 1.5.

pairs (I6···O2: 3.554 Å) to form a zigzag shaped and positive ribbon, and the inter-dimer hydrogen bonding pattern is $R_6^4(14)$, unlike the $R_4^2(10)$ pattern in **1** and **2**. The peripheral water molecules are *ca.* 0.28 Å and I^- anions 1.10 Å off the dimer's plane. The negative polyiodide ribbon in **3** is made up of zigzag shaped double-strand chains that are constructed from V shaped I_6^{2-} units. The I_6^{2-} units consist of two different linear I_3^- anions, one nearly symmetrical (I1–I2–I3, I–I 2.939 and 2.926 Å) and the another asymmetrical (I4–I5–I6, I4–I5 2.789 and I5–I6 of 3.167 Å), with an $I_3^-\cdots I_3^-$ distance of 3.642 Å. This assignment is based on the fact that I–I distances up to 3.6 Å correspond to bond energies at least half of that of I_2 so that they can be considered as I–I bonds.[12] To our best knowledge this type of I_6^{2-} species was only rarely observed before.[5,8,12] Although the rest of the I···I distances among the I_6^{2-} anions in the ribbon are close to 4.1 Å, the arrangement of I_6^{2-} anions is similar to that in **1** or **2**, that is, I_6^{2-} anions form a loosely linked zigzag chain, and two chains are twinned together. All iodine atoms are nearly coplanar in the polyiodide ribbon.

The association of both complementary, oppositely charged ribbons of one nanometer width, gives a stepped sheet (Fig. 4) because the positive and negative ribbons are not coplanar with *ca.* 1.1 Å separation between the two ribbons' planes. The positive and negative ribbons share arrays of I^- (I6) anions that are part of the I_6^{2-} units as well as the connectors of $(AdeH_2^{2+})_2$ dimers. There are a great many weak O–H···I and C–H···I hydrogen bonds at the interface of the counter-charged ribbons with lengths of 3.55–3.74 and 3.69–3.93 Å for O···I and C···I, respectively. They contribute to the formation of the sheet structures. The sheet structures further stack along the *b* direction to generate the 3D supramolecular architectures. As occurs in **1**, along the stacking direction, the positive and negative ribbons overlap alternately, and the remaining O–H donors of water molecules form O–H···I type hydrogen bonds between the sheets, with O···I ranging from 3.77–4.05 Å. The average separation between the adjacent sheets is about 3.6 Å, and the shortest intersheet I···I distance is 4.49 Å.

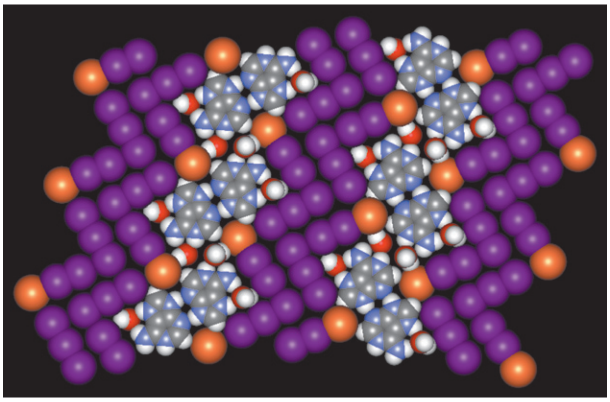


Fig. 4 One sheet composed of alternately arranged negative and positive ribbons in **3**. Color scheme: I purple and orange, Cl green; O red; N blue; C gray; H white. The orange-colored spheres are the I atoms shared by positive and negative ribbons.

Comparison of the structures: role of halides and nucleobases

In the previous paper[8] we described a 2D sheet of alternately arranged positive hydrogen-bonded cytosinium–water ribbons and negative polyiodide ribbons in $[CytH^+]_2(I_5^-)_2(H_2O)_3$ (Cyt = cytosine). In the sheet, the positive ribbon, built by water-bridged $[CytH^+]_2$ dimers, is straight. The associated polyiodide species is also, interestingly, a nearly straight shaped ladder of two interlocked branched polyiodide chains. In the current work, however, the zigzag shaped positive ribbons result in twinned zigzag polyiodide species. These results indicate the shape dependence and good adaptability of polyiodide species to the positive ribbons.

It is worth to compare the roles of halide atoms within the positive ribbon in the above three structures. In **1** and **2** the halide anions, Cl^- and Br^-, link the $(AdeH_2^{2+})_2$ dimers directly. The I···Cl and I···Br distances are 3.995 and 3.959 Å, respectively. They are slightly larger than the sum of the van der Waals radii (Bondi values, I···Cl 3.73 Å and I···Br 3.83 Å), indicating no I···Cl and I···Br bonding. In contrast, the I^- anions in **3** are assisted by water molecules to bridge $(AdeH_2^{2+})_2$ dimers, they are also part of the polyiodide ribbon. These observations obviously result from the fact that Cl^- and Br^- are better hydrogen-bond acceptors but have a lower tendency than I^- to form polyhalide species.

Nucleobases can adapt various protonated states, tautomers and different aggregates, which could be tuned by employing different amounts of H^+ and various acceptors.[6] In this work, bi-protonated $AdeH_2^{2+}$ cation is obtained by addition of excess acid in the reaction system. The cation has only one N site left as a hydrogen-bond acceptor. The $(AdeH_2^{2+})_2$ dimers, where two N acceptors of the two $AdeH_2^{2+}$ cations are used to form two intradimer hydrogen bonds, are complete hydrogen-bonding donors, and have a +4 charge. However, the dimers still form an extended hydrogen-bonded structure with the participation of other hydrogen-bonding acceptors like halide anions and water molecules. This work and the previously published results[8] demonstrate that the tendency to form extended aggregates through hydrogen bonds is the major difference of protonated nucleobases from many previously exploited templating cations,[4,5,12] which are usually considered to be discrete templates, and the inter-base hydrogen bonding seems not to be interrupted by polyiodide. These extended nucleobase aggregates display good size and interaction complementarity with polyiodide species, such as the orthogonal complementarity observed in $[AdeH^+](I_3^-)(I_2)_{5/2}(H_2O)$ and the parallel complementarity in $[CytH^+]_2(I_5^-)_2(H_2O)_3$[8] and the three architectures described here. The template effects induced by the extended hydrogen-bonded nucleobase ribbons to the formation and topology of the polyiodide species as well as the overall architectures are also well demonstrated in these structures. Therefore, the use of this new class of hydrogen-bonded template will allow new polyiodides of different and unexpected composition and topology, as well as novel supramolecular architectures to be obtained.

Finally, the three architectures are nanosized supramolecular structures built by ribbons of nanometer width. It is known that both linear hydrogen-bonded arrays of nucleobases, even DNA molecules, and some polyiodide chains exhibit interesting electrical behavior.[2,3,13,14] Thus, these architectures may be of interest to design and build electrical nano-devices, such as electron and proton nanowires or both. Especially, the sheet-like architectures may imply the possibility to build similar 2D nanosized arrays on surfaces, which may be of great interest for future research.

Conclusion

In this study three novel sheet-like supramolecular architectures were built from protonated adenine molecules and polyiodides. The adenine molecules are doubly protonated by addition of excess acid in the reaction system. The $\mathrm{AdeH_2}^{2+}$ cations form dimers through a pair of conventional N–H···N hydrogen bonds. These dimers further form 1D positive ribbons *via* halide anion bridges or iodide-water pairs. The positive ribbons, of zigzag shape and nanometer width, act as an extended hydrogen-bonded template to induce the zigzag shaped polyiodide ribbons composed of twinned zigzag polyiodide chains. The opposite charged ribbons build up 2D sheet-like structures of alternately arranged positive and negative strips of *ca.* 1 nm width. The architectures show good complementarity in the shape, size, charge and intercomponent interaction between the nanosized ribbons.

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