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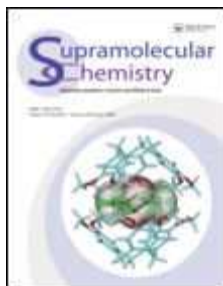
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<p>Note: The following files were submitted by the author for peer review, but cannot be converted to PDF. You must view these files (e.g. movies) online.</p> <p>Scheme 1.cdx Scheme 2.cdx Scheme 3.cdx</p>	



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**Imidazolium-Based Dicationic Cyclophanes. Solid-State Aggregates with
unconventional (C–H)⁺...Cl[−] Hydrogen Bonding Revealed by X-Ray Diffraction**

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Abstract

The first single-crystal X-ray crystallographic diffraction analysis of a dicationic heterophane showed a non-classic (C–H)⁺...Cl[−] hydrogen bond between the imidazolium rings and halide anions and the formation of unconventional charged assisted hydrogen bonds, which were the non-covalent forces driving the anion interactions shown by the dications **4·2X**. Here we report the halide-templated controlled synthesis and chemical response in basic media of **4·2X**. Their structural properties were examined at the gas phase by electrospray ionization mass spectrometry in the negative-ion mode and in the solid-state by X-ray crystallography. Thus, the negative-ion ESI-MS response showed that the formation of non-covalent self-aggregates of macrocyclic dications is a consequence of hydrogen-bonded complexes with halide anions. Notably, X-ray diffraction of dication **4a·2Cl·2H₂O** provides evidence for the H-bonding network, which has a crucial role in crystal

1
2 packing. The solid-state aggregates showed that chloride anions and water molecules
3
4 formed channels among dications **4a**⁺.
5

6
7 **Key words:** · charged cyclophanes · hydrogen bonds · anion recognition · templated
8
9 synthesis · electrospray mass spectrometry · X-ray diffraction crystallography ·
10
11

12 13 14 **Introduction**

15
16 Anion recognition chemistry includes current developments on anion-templated
17
18 synthesis and selective artificial anion receptors, especially positively charged systems
19
20 [1]. For these cationic or oligocationic hosts, the driving forces for binding are
21
22 electrostatic interactions or combinations with hydrogen bonding forces [2], i.e.
23
24 N-H...anion bonds [1a,3] and a novel type of charged hydrogen bonds (C-H)⁺...anion
25
26 [1j,3a,b,4,5,6d].
27
28

29
30 In the context of our current research on imidazolium-based frameworks, we
31
32 have studied cyclophanes **1·2X** and **2** [6b] together with dicationic pincers **3·2X**
33
34 (Figure 1) [6c]. Quaternary imidazolium units were selected due to their recognized
35
36 chemical stability [4,6-9]. Dicationic [14]imidazoliophanes **4·2X** are simple prototypes
37
38 for intermolecular interactions driven by unconventional (C-H)⁺...X hydrogen bond.
39
40 The significance of the hydrogen bonds in controlling the anion binding was observed
41
42 in solution by ¹H NMR in polar solvents [6d]. The '3+1' macrocyclization process is
43
44 template-controlled by chloride anions [8] (Figure 1). Dication **4a·2Cl·2H₂O** was the
45
46 first reported example of a non-classical (C-H)⁺...Cl⁻ hydrogen bond between the C-H
47
48 of the imidazolium rings and chloride anions in the solid state [4]. From dicationic
49
50 prototypes **4·2X**, a variety of imidazolium-linked scaffolds were investigated for anion
51
52 binding driven by this new type of (C-H)⁺...halide hydrogen bond.
53
54
55
56
57
58

59 **Figure 1**

60

1
2 The present paper deals with significant aspects of simple imidazolium-based
3
4 cyclophanes **4·2X**, such as halide template-directed '3+1' synthesis and the chemical
5
6 response in basic media. The structural properties are discussed with the data gained in
7
8 the solid state (X-ray crystallography) and the gas phase (electrospray ionization mass
9
10 spectrometry in the negative-ion mode).
11
12

13 14 15 16 **Results and Discussion**

17
18 We already reported the results obtained for halide template-directed synthesis:
19
20 the templated-controlled '3+1' macrocyclization reaction in the presence of chloride
21
22 anions. When 5 molar equiv of TBA·Cl were added to the reaction, the yield improved
23
24 to 83% for model dication **4a·2Cl**; competitive experiments indicate the relevance of
25
26 both the condensation step and the chloride-templated closure step [8]. However, the
27
28 '3+1' stepwise synthesis based on the coupling of protophane **5c** with 1,3-
29
30 bis(bromomethyl)-5-*tert*-butylbenzene **6** was not anion-dependent and the
31
32 macrocyclization reaction was governed by stereoelectronic control due to the *t*-butyl
33
34 group in protophane **5c** (Scheme 1).
35
36
37
38
39

40 **Scheme 1**

41
42 At this point, competitive experiments were set up between protophanes **5a** and
43
44 **5c** and 1,3-bis(bromomethyl)-*tert*-butylbenzene **6**—in both the absence and the
45
46 presence of TBA·Br (Scheme 2). The ratio of the macrocycles **4c·2Br** and **4d·2Br**
47
48 formed from the ¹H NMR analysis is shown in Scheme 2 and the results support the
49
50 idea of conformationally biasing assistance of the reaction leading to **4c·2Br**, not being
51
52 anion-controlled. Similar behavior was observed in the '3+1' approach leading to the
53
54 *N*-benzhydryl macrocyclic dications, precursors of azolophanes **1·2X** [6b]. The
55
56 enhancement induced by bromide anions for the formation of **4d·2Br** suggests a clear
57
58 anion-template influence for this macrocycle.
59
60

Scheme 2

Transformation of model dications **4a-c·2X** into the corresponding ureophanes was examined, since imidazolium subunit(s) on a variety of imidazolium-linked azolate betaines and azolyl salts, cyclophanes and pincers -*e.g.* **1·2X** to **4·2X**- have proved stable and no formation of by-products through generation of imidazol-2-ylidenes (NHC) has been detected to date [6,7]. From literature reports on benzimidazole pseudobases [10a], preparation of imidazol-2-ylidenes [10b] and transformations under basic conditions of 2,2'-diimidazolium [11a] and 2,2'-dibenzimidazolium salts located in either open-chain or macrocyclic systems [11b,c], we selected four methods: Method A [10a] KOH-H₂O/MeCN; Method B [10b] (i) *t*-BuOK/THF, (ii) *air*; Method C [11b] (i) 1,1',3,3'-tetramethylguanidine/MeCN-DMF, (ii) *air*; Method D [11b,c] (i) HNa/MeCN, (ii) *air* (Scheme 3).

Scheme 3

The chemical response of the *imidazolium rings* under basic reaction of dications **4a-c·2X** showed that in no instance was formation of products, through generation of carbenes such as ureophanes, detected (Scheme 3). Products of alteration or decomposition were observed by ¹H NMR and TLC, and these were not further investigated.

Structural Studies

Electrospray ionisation mass spectrometry is a consolidated as a innovative analytical technique, which normally involves the use of positive-ion ESI experiments [12a]. Recent negative-ion ESI-MS studies expand the current capacities of the negative-ion mode [12b-e]. Positive-ion electrospray ionization mass spectrometry was used for characterizing imidazolium-based frameworks, with prime examples derived from [1₄]metaheterophanes **1·2X** (**MH₂·2X**), **2** and **4·2X** (**M·2X**) [6b,9,13,14].

1
2 In the negative-ion mode ESI-MS experiments, we examined azolophanes **1·2X**
3
4 [13] together with a set of [{imidazolio}methyl] azolate betaines **B** and their
5
6 corresponding salts **BH·X** [7]. The negative-ion ESI responses displayed peaks
7
8 attributable to non-covalent self-aggregates: further study to confirm this was restricted
9
10 to instrumental limitation. Under the same experimental conditions [7,13], dications
11
12 **4a,c,d·2Cl** (**M·2Cl**) displayed different ionic species due to proton-mediated ion-
13
14 molecule reactions and non-covalent interactions, which produced several
15
16 polymolecular self-assemblies with chloride anions and the most characteristic species
17
18 corresponding to the singly charged ions $[M+3Cl]^-$, $[2M+5Cl]^-$ and $[3M+7Cl]^-$. Use of
19
20 a different mass spectrometer led to similar results: the negative-ion response between
21
22 dications **4a·2Cl** and **4a·2PF₆** revealed that in **4a·2Cl** (**M·2Cl**) a variety of self-
23
24 assembled aggregates were produced, whereas, on changing the counteranion, dication
25
26 **4a·2PF₆** (**M·2PF₆**) displayed a peak at m/z 145 from a PF_6^- anion due to the lack of
27
28 hydrogen bonding between the hexafluorophosphate counteranions and dications
29
30 (**4a**)²⁺ (Figure 2). Moreover, macrocycle **4b·2Cl** gave clean spectra and the base peak
31
32 corresponds to the single charged ion $[M+3Cl]^-$ (Figure 3). The negative-ion ESI-MS
33
34 response of dications **4a·2Cl**, **4a·2PF₆** and **4b·2Cl** shows that the formation of non-
35
36 covalent self-aggregates in the gas phase is a consequence of hydrogen-bonded
37
38 complexes with chloride anions.
39
40
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42
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46

47 **Figure 2**

48
49 **Figure 3**

50
51 ¹H NMR spectroscopy studies indicated the importance of imidazolium units as
52
53 motifs for anion recognition of **4·2X** and complexation studies with the model dication
54
55 **4c·2PF₆** using several tetrabutylammonium salts (**TAB·X**) in polar solvents (CD_3CN
56
57 and $DMSO-d_6$) were performed. The best association constant (K_a) was observed for
58
59 the complex of **4c·2PF₆** and **TBA·CH₃CO₂** in $DMSO-d_6$ [6d].
60

1
2 One of the relevant aspects of model imidazolium-based cyclophanes **4·2X** is
3
4 the solid-state aggregates with unconventional C–H...Cl[−] hydrogen bonds observed by
5
6 X-ray crystallography. Among the whole palette of hydrogen bonds [3a], the first non-
7
8 classic (C–H)⁺...Cl[−] hydrogen bonds between quaternary imidazolium rings and the
9
10 counteranions were observed for dicationic imidazoliophane **4a·2Cl·2H₂O** in the solid
11
12 state [4,14,15a]. Thereafter, a variety of quaternary imidazolium-linked frameworks
13
14 were reported for anion recognition driven by (C–H)⁺...X[−] hydrogen bonds [1j,3a,b,5].
15
16 The imidazolium units represent the main structural motifs for intermolecular
17
18 interactions driven by hydrogen bonds in which the chloride counteranions have been
19
20 noncovalently bound to the dicationic framework and, in addition, the C–H...O
21
22 hydrogen bonds with water play a role in governing the conformations of the solid-state
23
24 aggregates. In this connection, Steiner has pointed out that hydrogen bonds from C–H
25
26 groups to halides ions are only rarely discussed in the literature, even though stronger
27
28 C–H donors had CH...Hal[−] distributions of a similar shape as O/N–H donors had and
29
30 can be analyzed in the same way. As for (NN)Csp²–H fragment, the mean C–H... Cl[−]
31
32 distance of 2.54 Å was found [3c]. Within NH...Hal[−] bonds, we should mention the
33
34 calix[4]pyrroles reported by Sessler and co-workers as chloride anion receptors [3c,16]
35
36 and also showing imidazolium inclusion in both the confused and regular forms
37
38 [3a,3b].
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40
41
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46
47

48 From the present single-crystal X-ray diffraction analyses of two macrocyclic
49
50 dications [15a], relevant aspects should be mentioned. Their molecular shapes are
51
52 shown in Figure 4: Dication **4a** assumes a chair-like conformation in contrast with the
53
54 cone-like arrangement observed for **4b**. However, both dications **4a** and **4b** have
55
56 similar molecular cavity dimensions, a square of 5 Å side, close to those observed for
57
58 macrocyclic bis-betaines **2** and related systems [6b].
59
60

Figure 4

1
2 For dication **4a**·2Cl·2H₂O, the non-covalent interactions with the chloride ions
3
4 are based on multi-centered (C–H)⁺···Cl bonds established between the Cl[–] ion with
5
6 the aromatic hydrogen bonds on the *m*-xylyl spacer and the acidic hydrogen atom of
7
8 the imidazolium ring which is the shortest hydrogen bond interaction (2.54(2) Å, θ =
9
10 157(1)°) consistent with the complexing ability of chloride anions; there are, in
11
12 addition, weak interactions with water. The chloride anions occupy an outer position
13
14 above and below the main plain defined by the methylene spacer groups (see later).
15
16 For the X-ray diffraction analysis of **4b**·2Cl·3.5H₂O·0.5CH₃CN, many different
17
18 crystals were used but crystals deteriorated so fast that, in consequence, the final
19
20 refinement values were inappropriate for a detailed discussion of non-covalent
21
22 interactions.
23
24
25
26
27

28 For the X-ray analysis of **4a**·2Cl·2H₂O, a perspective molecular diagram of
29
30 dication **4a** is shown in Figure 5 and selected nonbonding parameters related to the
31
32 molecular shape as well as the H-bonding interactions are listed in Tables 1 and 2.
33
34 Since the molecule is a centrosymmetric structure, the experimental asymmetric unit
35
36 contains a half molecule of dication **4a** and one chloride anion and one water molecule,
37
38 matched by an equivalent subunit generated by symmetry. The atom numbering
39
40 diagram used for the X-ray data [15b] is not the same as the IUPAC numbering system
41
42 for the NMR data. Significant nonbonding distances [Å] concern both the (C–H)⁺···Cl[–]
43
44 interactions and the molecular shape adopted by the dicationic framework that may be
45
46 described by the macrocyclic cavity dimensions, the spatial arrangement within the
47
48 four rings which constitute the walls of the dicationic framework and their inclination
49
50 with respect to the reference plane. The weighted least-squares reference plane defined
51
52 by C7, C11, C7a, and C11a methylene carbon atoms are C7·····C1 = 4.954(3) Å and
53
54 C(7)·····C(11a) = 4.996(3) Å, with the cavity dimensions being a square of *ca.* 5 Å side
55
56 (Table 1).
57
58
59
60

Figure 5**Table 1**

A relevant point relating to the structural shape of dication **4a** is the position of the corresponding counteranions within the molecule: the two chloride anions are located above and below the reference plain (plane E). The chloride counteranion is bi-centered between the acidic hydrogen atom on the imidazolium ring, i.e. H10, which is the shortest hydrogen bond interaction and a *m*-xylyl hydrogen atom, i.e. H6. The H...Cl⁻ distances (Å) and (C-H)⁺... Cl⁻ angles (°) are H6...Cl1 = 2.81(2) Å, angle 162.(1)° and H10...Cl1 = 2.54(2) Å, angle 157.(1)°; for the *weak* interactions with water, the C-H...O hydrogen bonding connects the trifurcated acceptor O1 with the cationic ring, as shown in Figure 5 (Tables 1 and 2).

Table 2

The unit cell packing of dication **4a·2Cl·2H₂O** contains two independent cations together with their associated anions and four water molecules located in a channel fashion. The hydrogen bond networks help to sustain the crystal lattice and forming channels that extend through the crystal: the chloride anions and the water molecules are located among the dicationic imidazolium-based framework in a channel disposition, as shown in Figures 5 and 6. On examination of the crystal packing, intermolecular π - π stacking interactions between the *m*-xylyl aromatic rings also help sustain the crystal lattice: the rings are positioned at an interplanar distance of 3.59 Å and engaged in a parallel displaced pattern, whereas the interplanar separations between the imidazolium rings are in the range of 5 Å to 8.5 Å.

Figure 6

For the X-ray analysis of **4b·2Cl·3.5H₂O·0.5CH₃CN**, we measured several sets of data and used many different crystals, but as crystals deteriorated fast, it was difficult to find reliable solutions for the ordered fragments. The disordered Cl⁻ anions

1 and solvent atoms were unidentifiable in most of the collected data. In the end, we
2
3
4 reached a physically and chemically acceptable solution, refined to a reasonable point
5
6 that took into consideration both the presence of structural disorder and rapid crystal
7
8 deterioration; the best recorded data were then refined to $R_1 = 0.1032$ and $wR_2 =$
9
10 0.2512 . The asymmetric unit contains two crystallographically independent dications
11
12 (**4b**), molecule **A** and molecule **B**, their four associated chloride anions together with
13
14 seven water molecules and one solvent molecule (acetonitrile) (Figure 7). Molecule **A**
15
16 tended to form a three-centered hydrogen bond with one of the chlorine counteranions
17
18 Cl2 and molecule **B** preferred to hydrogen bond to an included water molecule.
19
20 Although both **A** and **B** molecules displayed uncommon multi-centered acceptor
21
22 hydrogen bond arrangements mainly due to the presence of hydrogen donor-rich
23
24 imidazolium rings, these similar complexing patterns show how sensitive the (C-
25
26 H)⁺...*Acceptor* hydrogen bond is to structural changes within the imidazolium-based
27
28 framework.
29
30
31
32
33

34 35 **Figure 7**

36
37 In relation with the structural effect, we should mention that Baker *et al.* [17]
38
39 have reported a tricationic imidazolium-based cyclophane formed by two mesitylene
40
41 rings triple-bridged by three imidazolium rings **M·3Br·2H₂O** and that X-ray
42
43 diffraction analysis revealed that in each molecule the three bromide anions formed a
44
45 hydrogen bond with two water molecules and no anionic species are trapped within the
46
47 imidazoliophane.
48
49
50

51 52 53 **Conclusions**

54
55 Dicationic [1₄]imidazoliophanes **4·2X** are simple prototypes for examination of
56
57 the intermolecular interactions driven by hydrogen bonds, in which the halide
58
59 counteranion, i.e. X=Cl, was non-covalently bound to the macrocyclic framework and,
60

1
2 in addition, the ability to bind halide anions was exploited during their synthesis. The
3
4 chemical responses of *imidazolium* rings for dications **4a-c·2X** in basic media were
5
6 examined and the putative formation of products through generation of imidazol-2-
7
8 ylidenes (NHC), *e.g.* ureophanes, was not detected. Their distinctive structural facets
9
10 were examined in the gas phase by electrospray ionization mass spectrometry in
11
12 negative-mode experiments and in the solid-state by X-ray crystallography of
13
14 **4a·2Cl·2H₂O** and **4b·2Cl·3.5H₂O·0.5CH₃CN**.
15
16
17

18
19 On the whole, the simple imidazolium-based cyclophanes **4·2X** can be
20
21 considered models for intermolecular anion interactions driven by hydrogen bonds
22
23 since there is good parallelism between the experimental trends observed in the solid
24
25 state, in the gas phase by negative-ion ESI-MS and in solution by ¹H NMR
26
27 complexation studies. Notably, the single-crystal X-ray diffraction analysis of dication
28
29 **4a·2Cl·2H₂O** typified the first example of a non-classic (C–H)⁺...Cl⁻ hydrogen bond
30
31 between the imidazolium rings and chloride anions —the shortest hydrogen bond
32
33 interaction was H10...Cl1 (2.54 Å, θ = 157°). Efforts are currently being directed
34
35 towards the use of imidazolium-linked systems for processes controlled by hydrogen
36
37 bonding networks.
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39
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45 Experimental Section

46
47 **General Methods:** ¹H NMR: Varian Gemini 200 and Varian Gemini 300
48
49 spectrometers (200 MHz and 300 MHz). NMR spectra were determined in
50
51 dimethylsulfoxide-*d*₆ or chloroform-*d*, and chemical shifts are expressed in parts per
52
53 million (δ) relative to the central peak of dimethylsulfoxide-*d*₆ or chloroform-*d* at
54
55 298°K. TLC was performed on Merck pre-coated 60 F₂₅₄ silica gel plates in the solvent
56
57 system methanol-ammonium chloride 2M-nitromethane (6:3:1) as developing solvent;
58
59 and the spots were located with UV light and developed with a 10% aqueous solution
60

of potassium iodide or 3% aqueous solution of hexachloroplatinic acid. When a rotary evaporator was used, the bath temperature was 25°C. In general, the compounds were dried overnight at 25°C in a vacuum oven.

Materials: 1,1',3,3'-Tetramethylguanidine and tetrabutylammonium salts were purchased from commercial sources. Macrocycles **4a-c·2X** [6d,14], protophanes **5a,c** [6d,14], and 1,3-bis(bromomethyl)-5-*tert*-butylbenzene (**6**) [18] were prepared as described in the literature.

Macrocycle **4c·2Br**. Anion Template Effect.

Experiment 1: (Scheme 1) A stirred solution of 1,3-bis(bromomethyl)-5-*tert*-butylbenzene (**6**, 0.31 g, 0.96 mmol) in dry acetonitrile (50 mL) was added dropwise to a solution of protophane **5c** (0.5 g, 0.96 mmol) in dry acetonitrile (150 mL) at 25°C under nitrogen, and the mixture was then maintained in a bath at about 85°C for 48 h. The solvent was removed in a rotary evaporator, and the solid residue was triturated with dry acetone (25 mL) and filtered to give macrocycle **4c·2Br** (0.45 g, 56%) as a white solid. ¹H NMR (200 MHz, CDCl₃): δ = 0.90-0.97 (m, 12 H), 1.35-1.48 (m, 36 H), 2.55-2.62 (m, 8 H), 5.48 (s, 8 H), 6.42 (s, 2 H), 7.32 (s, 4 H), 10.75 (s, 2 H) ppm.

Experiment 2: (Scheme 1) A stirred solution of 1,3-bis(bromomethyl)-5-*tert*-butylbenzene (**6**, 0.31 g, 0.96 mmol) in dry acetonitrile (50 mL) was added dropwise to a solution of protophane **5c** (0.5 g, 0.96 mmol) and 5 molar equiv of tetrabutylammonium bromide (1.5 g, 4.8 mmol) in dry acetonitrile (150 mL) at 25°C under nitrogen, and the mixture was then maintained in a bath at about 85°C for 48 h. The solvent was removed in a rotary evaporator, and the solid residue was triturated with dry acetone (25 mL) and filtered to give macrocycle **4c·2Br** (0.44 g, 55 %) as a white solid.

1
2 **Experiment 3:** (Scheme 1) A stirred solution of 1,3-bis(bromomethyl)-5-*tert*-
3 butylbenzene (**6**, 61 mg, 0.19 mmol) in dry acetonitrile (14 mL) was added dropwise to
4
5 a solution of protophane **5c** (0.1 g, 0.19 mmol) and 5 molar equiv of
6
7 tetrabutylammonium hexafluorophosphate (0.31 g, 0.95 mmol) in dry acetonitrile (25
8
9 mL) at 25°C under nitrogen, and the mixture was then maintained in a bath at about
10
11 85°C for 48 h. The solvent was removed in a rotary evaporator, and the solid residue
12
13 was triturated with dry acetone (10 mL) and filtered to give macrocycle **4c·2X** (71 mg,
14
15 39-45 %) as a white solid.
16
17
18
19
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23

24 **Competitive experiments combining protophanes 5a and 5c and 1,3-**
25 **bis(bromomethyl)-5-*tert*-butylbenzene 6.**

26 **Experiment 1:** (Scheme 2) A stirred solution of 1,3-bis(bromomethyl)-5-*tert*-
27 butylbenzene (**6**, 61 mg, 0.19 mmol) in dry acetonitrile (14 mL) was added dropwise to
28
29 a solution of protophane **5a** (46 mg, 0.19 mmol) and protophane **5c** (0.1 g, 0.19 mmol)
30
31 in dry acetonitrile (25 mL) at 25°C under nitrogen, and the mixture was then
32
33 maintained in a bath at about 85°C for 48 h. The solvent was removed in a rotary
34
35 evaporator, and the solid residue was triturated with dry acetone (10 mL) and filtered.
36
37 According to the ¹H NMR analysis, the reaction mixture composition led to the
38
39 formation of macrocycles **4c·2Br:4d·2Br** in the proportion of 1.6:1.4. **4c·2Br** ¹H NMR
40
41 (300 MHz, DMSO-*d*₆): δ = 0.67-0.72 (m, 12 H), 0.82-0.86 (m, 8 H), 1.07-1.14 (m, 8
42
43 H), 1.34 (s, 18 H), 2.21-2.26 (m, 8 H), 5.50 (s, 8 H), 6.45 (s, 2 H), 7.70 (s, 4 H), 9.40
44
45 (s, 2 H) ppm. **4d·2Br** ¹H NMR (300 MHz, DMSO-*d*₆): δ = 1.31 (s, 9 H), 5.42 (s, 4 H),
46
47 5.43 (s, 4 H), 6.72 (s, 1 H), 7.02 (s, 1 H), 7.56-7.60 (m, 5 H), 7.82 (s, 4 H), 9.36 (s, 2
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49 H) ppm.
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Experiment 2: (Scheme 2) A stirred solution of 1,3-bis(bromomethyl)-5-*tert*-
butylbenzene (**6**, 61 mg, 0.19 mmol) in dry acetonitrile (14 mL) was added dropwise to

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2 a solution of protophane **5a** (46 mg, 0.19 mmol), protophane **5c** (0.1 g, 0.19 mmol) and
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4 5 molar equiv of tetrabutylammonium bromide (0.31 g, 0.95 mmol) in dry acetonitrile
5
6 (25 mL) at 25°C under nitrogen, and the mixture was then maintained in a bath at
7
8 about 85°C for 48 h. The solvent was removed in a rotary evaporator, and the solid
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10 residue was triturated with dry acetone (10 mL) and filtered. According to the ¹H NMR
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12 analysis, the reaction mixture composition led to the formation of macrocycles
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14 **4c·2Br:4d·2Br** at the proportion of 1.25:1.75.
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21 **Attempted preparation of ureophanes.**

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23 **Experiment 1. Method A.** A suspension of macrocycle **4a·2PF₆** (100 mg, 0.16
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25 mmol) and finely powdered 85% potassium hydroxide (21 mg, 0.32 mmol) in dry
26
27 acetonitrile (20 mL) was vigorously stirred at room temperature for 3 h and at reflux
28
29 temperature for 3 d. The suspension was cooled and filtered, and the solution was
30
31 evaporated to dryness to obtain alteration or decomposition products.
32
33

34
35 **Experiment 2. Method B.** A solution of sublimate potassium *tert*-butoxide (121 mg,
36
37 1.08 mmol) in dry THF (20 mL) was added dropwise to a suspension of macrocycle
38
39 **4b·2PF₆** (200 mg, 0.27 mmol) in dry THF (80 mL), under an atmosphere of nitrogen.
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41 After the reaction mixture was stirred at room temperature for 5 h, the mixture was
42
43 heated at reflux temperature and dry air was bubbled through for 16 h. The resulting
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45 suspension was evaporated to dryness to obtain alteration or decomposition products.
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50 **Experiment 3. Method C.** A suspension of macrocycle **4a·2Cl** (186 mg, 0.45 mmol)
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52 and 1,1',3,3'-tetramethylguanidine (0.5 mL, 3.99 mmol) in a dry mixture of
53
54 acetonitrile and dimethylformamide (5 mL, 1:1) was stirred at reflux temperature and
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56 dry air was bubbled through for 21 h. The reaction mixture was cooled and evaporated
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58 to dryness to recover macrocycle **4a·2Cl**.
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1
2 **Experiment 4. Method D.** A mixture of macrocycle **4a·2Cl** (200 mg, 0.48 mmol) in
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4 dry acetonitrile (35 mL) was added dropwise to a suspension of NaH (288 mg, 12
5
6 mmol) in dry acetonitrile (20 mL). After the reaction mixture was stirred at room
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8 temperature for 4 h, dry air was bubbled through for 18 h. The resulting suspension
9
10 was evaporated to dryness to obtain alteration or decomposition products.
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13 14 15 16 **Electrospray Ionization Mass Spectrometry.**

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18 The negative-ion ESI-MS experiments were first performed on a VG-Quattro mass
19
20 spectrometer from Micromass Instruments, as previously described [7,13]. Then,
21
22 negative-ion ESI-MS analyses were recorded on a ZQ mass spectrometer from Waters-
23
24 Micromass. Electrospray interface (pneumatically assisted) under the following
25
26 conditions: the nebulizing nitrogen gas flow was 30 L h⁻¹ and drying nitrogen 250 L h⁻¹,
27
28 source temperature 80°C with a capillary voltage of -2.5 kV and the cone voltage
29
30 varied from 20V to 80V depending on the experiment. The eluent flowing through the
31
32 probe was CH₃CN:H₂O (1:1, v/v) at a flow rate of 100 μL min⁻¹. Spectra were scanned
33
34 at a rate of 1.5 s over the mass range *m/z* 10-1500 and were recorded and processed
35
36 using the MassLynx software, version 4.0. Mass calibration was performed with a
37
38 NaCsI mixture standard solution.
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48 **Single-crystal X-ray diffraction analysis.**

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50 Registration no. CCDC 182/1132 contains the supplementary crystallographic data for
51
52 this paper. *Imidazoliophanes 4a·2Cl·2H₂O* and *4b·2Cl·3.5 H₂O·0.5CH₃CN*: CCDC
53
54 deposition numbers 102466 and 102467.
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58

59 **Acknowledgments**

60
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1
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4 2005SGR00158, (*Generalitat de Catalunya*).
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Captions to Tables, Schemes and Figures

Table 1. Selected X-ray crystallographic data for macrocycle **4a·2Cl·2H₂O**.^{a,b}

^aCCDC 182/1132. ^bX-ray atom numbering diagram. ^cMost relevant intermolecular distances. ^dDihedral angles between the weighted least-squares planes. Plane A: C1-C2-C3-C13-C12-C6, Plane B: N1-C10-N2-C9-C8, Plane C: C1a-C2a-C3a-C13a-C12a-C6a, Plane D: N1a-C10a-N2a-C9a-C8a, Plane E: C7-C11-C7a-C11a. ^eDistance between the indicated planes. ^fDistance between the chloride anion and the indicated plane.

Table 2. Hydrogen-bonding geometry [Å or °]

Scheme 1. “3 + 1” Convergent synthesis of **4c·2Br**.

Scheme 2. Competitive experiments combining trinuclear protophanes **5a** and **5c** and bis(bromomethyl)-*tert*-butylbenzene **6** to build [1₄]imidazoliophanes **4c·2Br** and **4d·2Br**, showing the ratio of the macrocycles formed.

Scheme 3. Chemical response of dications **4a-c·2X**. *Reagents and Conditions*. Method A: (i) 10 eq KOH-H₂O/MeCN, rt 3h; (ii) reflux 3 days. Method B: (i) Sublimate *t*-BuOK/THF/N₂, 5h, (ii) *air*, reflux 16h. Method C: (i) 1,1',3,3'-tetramethylguanidine/dry MeCN-DMF, (ii) *air*, rt 24h, 80 °C 21h. Method D: (i) HNa/dry MeCN, Ar, rt 4h (ii) *air*, rt 18h.

Figure 1. Imidazolium molecular motifs in [1₄]metaheterophane frameworks.

Figure 2. Negative-ion ESI-MS of **4a·2Cl** and **4a·2PF₆**.

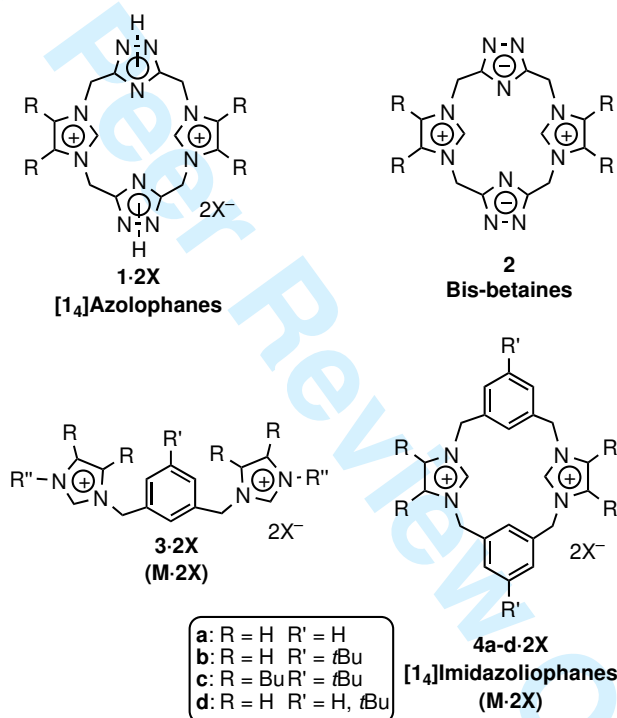
Figure 3. Negative ion ESI-MS of **4b·2Cl**.

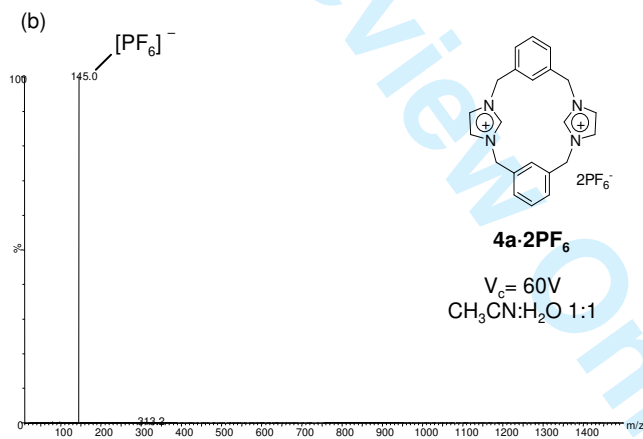
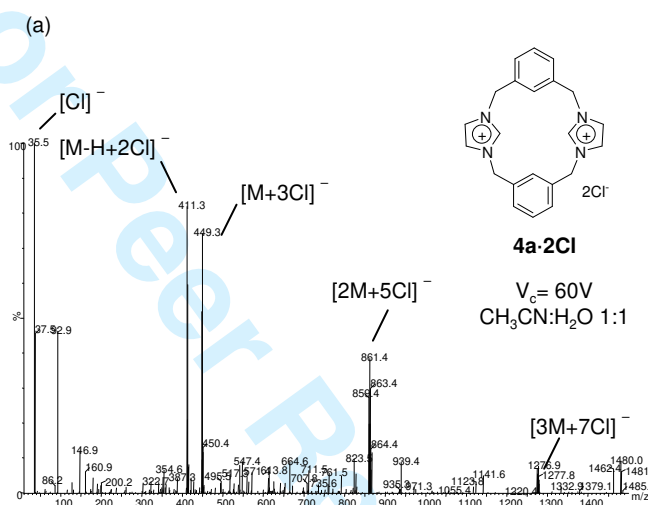
Figure 4. Molecular shape of dications **4a·2Cl·2H₂O** and **4b·2Cl·3.5H₂O·0.5CH₃CN**.

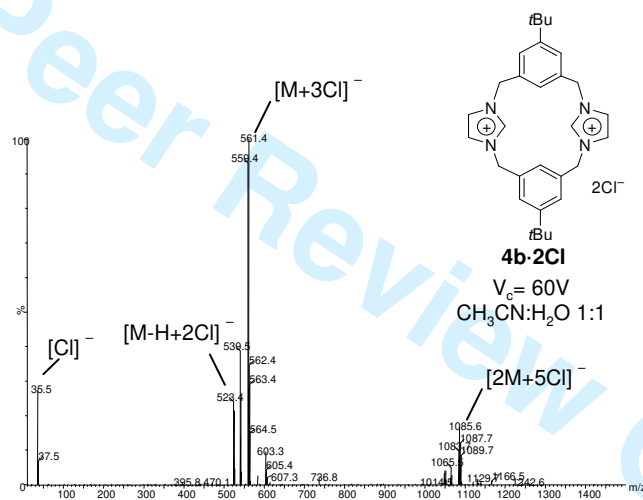
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2 **Figure 5.** Imidazolium-based dication $4a \cdot 2Cl \cdot 2H_2O$: Molecular structure showing
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4 non-classic $(C-H)^+ \cdots Cl^-$ hydrogen bonds; crystal packing showing a channel
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6 disposition of the chloride anions and the water molecules among the dicationic
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8 framework.
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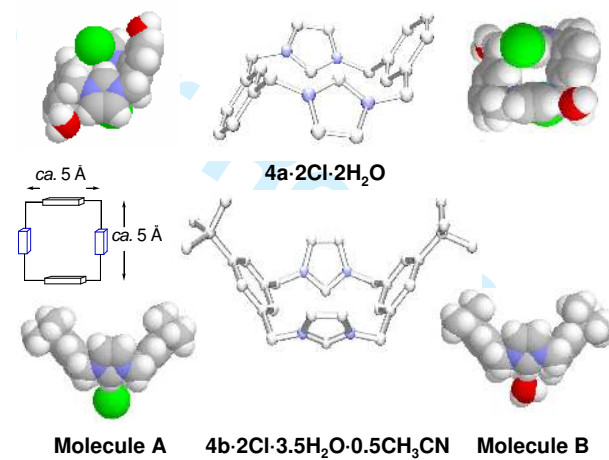
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11 **Figure 6.** Crystal packing of dication $4a \cdot 2Cl \cdot 2H_2O$.
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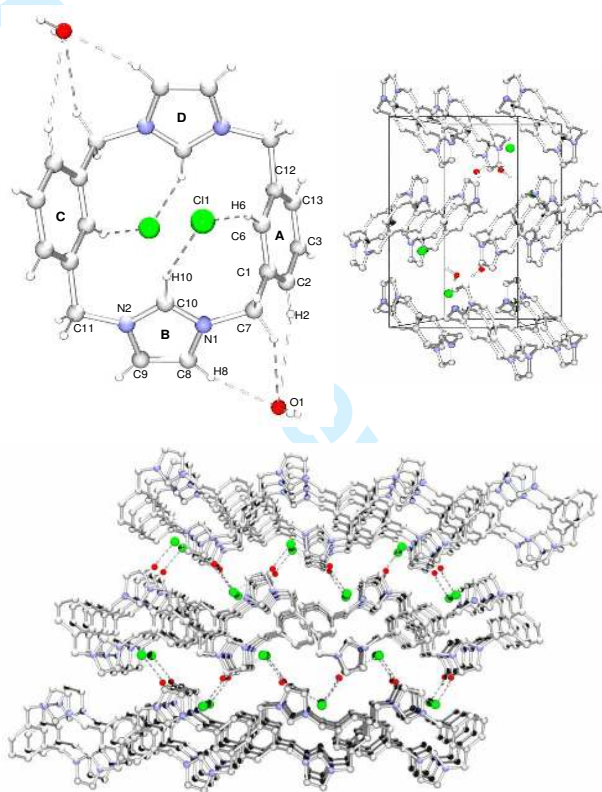
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14 **Figure 7.** Dicationic macrocycle $4b \cdot 2Cl \cdot 3.5H_2O \cdot 0.5CH_3CN$.
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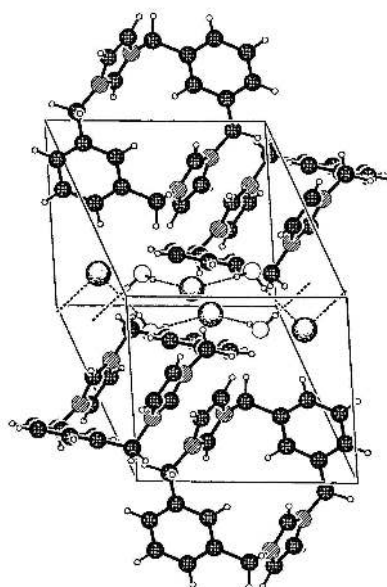


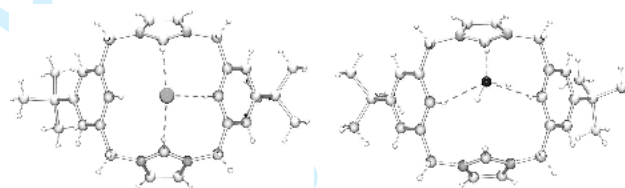




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Molecule A

Molecule B

