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Multifunctional Organosulfonate Anions Self-Assembled with Organic Cations by Charge-Assisted Hydrogen Bonds and the Cooperation of Water

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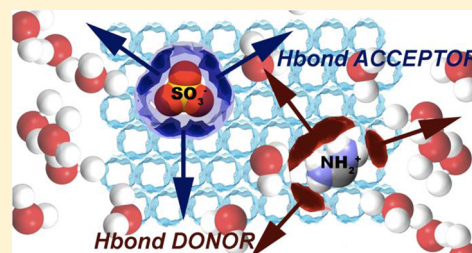
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S Supporting Information

ABSTRACT: The present study focuses on the assembly of organo-cations with organo-anions in water. The anions, characterized by symmetric moieties (carbon-, adamantane-, or calixarene-based) functionalized with directional hydrogen bond (HB) acceptor functions (tetra-sulfonate moieties), are combined with planar guanidinium or terephthalimidamide cations as hydrogen bond donors, the purpose being to integrate water molecules into the lattice. The imbalance between the charge on the two components, and the considerable number of HB donor and acceptor sites, promotes the insertion of water into the structures. In the reported structures, a part of the water molecules serves as a structural linker between the anions and cations, while the remaining molecules cluster into channels and cavities in a loose association with the supramolecular matrix framework.



INTRODUCTION

Fully organic ionic solids integrate electrostatic interactions with hydrogen bonding (HB),^{1–5} weak interactions,^{6,7} and shape factors to sustain crystal assemblies.^{8,9} Thus, organic molecules of opposite charge promote the formation of supramolecular buildings where electroneutrality and stoichiometry are dominant structure-directing features.^{10–13} The self-assembly of charged organic molecules^{14–16} for the formation of crystalline architecture is based on the coupling of complementary charged functionalities,^{17,18} such as carboxylate^{19–24} and sulfonate anions^{25–28} with ammonium,²⁹ or sulfonate³⁰ with other organo-cations. In this context, a wide range of two-component supramolecular structures^{25,28,31,32} has been fabricated, especially during the past few years. The construction of complex crystal architectures implies both the multiplication of organic functionalities on the same molecule and control over their space orientation.^{33–35} The degree of complexity increases progressively with the use of multidentate molecular struts combined with the planar and three-dimensional (3D) geometries of the components.

The probability of hydrate formation is enhanced by introducing multiple functionalities, especially when there is an uneven number of HB donors and acceptors, as well as increased molecule complexity, which promotes ineffective packing.^{36–38} Moreover, the ionic nature of organic moieties makes them compatible with aqueous media, feeding the structure with water as an additional and constructive building element.^{30,38–41} From the applicative point of view, hydrate formation is a central issue in pharmaceutical applications,^{42,43}

providing enhanced solubility, stability, and response to the environment compared to the anhydrous precursors.

The water molecules contained in the lattice can usually be divided into two categories with two different roles: one is structural, the water molecules serving to sustain the lattice architecture, and the second relates to the occupation of cavities formed by hydrogen bonded components.¹⁹ Accordingly, channels, pores, and discrete pockets contain water in clusters of different sizes.⁴⁴ In the present work, while investigating the aggregation of organic molecules bearing multiple charges, we found interesting hydrated structures and discriminated between hard and soft host/water interactions. We were intrigued by the 3D geometries of the building blocks and explored a few polyfunctional organosulfonates self-assembled with mono- or organo-dications (Scheme 1). Our investigation encompassed tetrahedral and conical orientation of the sulfonate groups. We obtained six charge-assisted hydrogen bonded organic frameworks, which were studied by spectroscopic techniques (¹H NMR, IR) and thermal methods (thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC)). Crystals suitable for conventional and synchrotron radiation X-ray diffraction characterization were grown from aqueous media, and their single crystal X-ray structures were determined. The comparison of the structural features of these charge-assisted systems allowed us to highlight

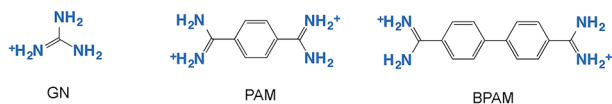
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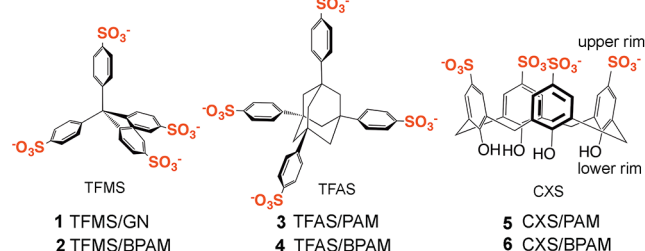
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Scheme 1. Schematic Representation of Anionic (Red)/Cationic (Blue) Components Used To Synthesize Charged Organic-Molecule Suprastructures

CATION



ANION



75 the role of multidentate charged molecules in the formation of
76 structures, and the tendency to integrate matrix and water
77 molecules into crystal architectures.

78 ■ EXPERIMENTAL SECTION

79 4,4',4'',4'''-Methanetetrayltetrabenzenesulfonic acid (H_4 TFMS),
80 4,4',4'',4'''-(adamantane-1,3,5,7-tetrayl)tetrabenzenesulfonic acid
81 (H_4 TFAS), terephthalimidamide hydrochloride (PAM-HCl), and
82 [1,1'-biphenyl]-4,4'-bis(carboximidamide) dihydrochloride (BPAM-
83 2HCl) were prepared as previously described, or as reported in the
84 literature, and used in their protonated forms.^{45–48} Guanidinium
85 hydrochloride (GN-HCl), 4-sulfocalix[4]arene (H_4 CXS), and all
86 solvents used for synthesis, and crystallization were commercially
87 available and used as received. NMR spectra were recorded on Bruker
88 AVANCE III (400 MHz). Chemical shifts (δ) for 1H spectra were
89 referenced using internal solvent resonances and are reported relative
90 to tetramethylsilane (TMS). According to 1H NMR, the ratio between
91 cationic and anionic components is easily evaluated, and the amount of
92 water in the molecular adduct is calculated by subtracting the one
93 found in the deuterated solvent considered as blank. Fourier transform
94 infrared (FT-IR) spectra (4000–700 cm^{-1}) were recorded on a
95 Nicolet Nexus spectrophotometer equipped with a Smart Orbit HATR
96 accessory (diamond crystal). DSC data were recorded on a Mettler
97 Toledo Stare DSC1 analysis system equipped with low temperature
98 apparatus. The experiments were run under nitrogen atmosphere in
99 standard 40 μL Al pans. The DSC analyses were performed from 25 to
100 200 $^{\circ}C$ (10 $^{\circ}C/min$) to study the transformation related to water and
101 solvent molecule loss, and to compare them to crystal structure
102 information. TGA was collected on a PerkinElmer instrument
103 (samples mass approximately 5–10 mg) from 25 to 400 $^{\circ}C$ under
104 nitrogen flow (80 mL/min). See [Supporting Information](#) for details on
105 1H NMR and IR spectroscopy, TGA, and DSC analysis.

106 **Synthesis.** *Synthesis of 1.* H_4 TFMS (27.4 mg, 0.032 mmol)
107 dissolved in 0.5 mL of MeOH was gently added to a solution of GN-
108 HCl (12.2 mg, 0.128 mmol) in 0.5 mL of MeOH in an open vial. After
109 24 h, white crystals suitable for X-ray data collection were obtained
110 from the solution, corresponding to (GN)₄(TFMS)·8H₂O (1). The
111 solid was filtered out and vacuum-dried (17 mg, yield 62%).

112 *Synthesis of 2.* H_4 TFMS (20.5 mg, 0.024 mmol) was dissolved in a
113 mixture of 0.1 mL of NaOH (1 M), 0.9 mL of water, and 3.0 mL of
114 THF. To the mixture, BPAM·2HCl (14.9 mg, 0.048 mmol) dissolved
115 in 1 mL of water and 2.5 mL of THF was added. After 24 h, light
116 yellow crystals suitable for X-ray data collection were obtained from
117 the solution, corresponding to (BPAM)₂(TFMS)·13H₂O (2). The
118 solid was filtered out and vacuum-dried (17 mg, yield 67%).

119 *Synthesis of 3.* H_4 TFAS (18.4 mg, 0.024 mmol) was dissolved in a
120 mixture of 0.1 mL of NaOH (1 M), 0.9 mL of water, and 1.0 mL of
121 EtOH. To the mixture, PAM-HCl (11.3 mg, 0.048 mmol) dissolved in

1.0 mL of water and 1.0 mL of EtOH was added. After 24 h, white
122 crystals suitable for X-ray data collection were obtained from the
123 solution, corresponding to (PAM)₂(TFAS)·9H₂O (3). The solid was
124 filtered out and vacuum-dried (16 mg, yield 63%).
125

Synthesis of 4. H_4 TFAS (9.2 mg, 0.012 mmol) was dissolved in a
126 mixture of 0.05 mL of NaOH (1 M), 0.45 mL of water, and 2.0 mL of
127 MeOH. To the mixture, BPAM·2HCl (7.5 mg, 0.024 mmol) dissolved
128 in 0.5 mL of water and 1 mL of MeOH was added. After 24 h, white
129 crystals suitable for X-ray data collection were obtained from the
130 solution, corresponding to (BPAM)₂(TFAS)·6.4H₂O·3.6MeOH (4).
131 The solid was filtered out and vacuum-dried (12 mg, yield 78%).
132

Synthesis of 5. H_4 CXS (17.8 mg, 0.024 mmol), dissolved in 0.4 mL
133 of water and 0.5 mL of MeOH, was gently added a solution of PAM-
134 HCl (11.3 mg, 0.048 mmol) in 0.75 mL of water. After 24 h, white
135 crystals suitable for X-ray data collection were obtained from solution,
136 corresponding to (PAM)₂CXS·4H₂O·0.5MeOH (5). The solid was
137 filtered out and vacuum-dried (16 mg, yield 64%).
138

Synthesis of 6. H_4 CXS (8.9 mg, 0.012 mmol) dissolved in 0.5 mL
139 of water and 1.0 mL of MeOH, was gently added to a solution of
140 BPAM·2HCl (7.5 mg, 0.024 mmol) dissolved in 0.5 mL of water and 1
141 mL of MeOH. After 24 h, white crystals suitable for X-ray data
142 collection were obtained from the solution, corresponding to
143 (BPAM)₂(CXS)·8H₂O·2CH₃OH (6). The solid was filtered out and
144 vacuum-dried (12 mg, yield 79%).
145

X-ray Diffraction. A summary of data collection and structure
146 refinement for 1–6 is reported in the [Supporting Information Table](#)
147 [S3](#). Single crystal data for 1, 3, and 6 were collected with a Bruker
148 Smart APEXII at 200 K, whereas data for 2 were collected with a
149 Bruker D8 PhotonII at 100 K, Mo $K\alpha$: $\lambda = 0.71073$ Å. The intensity
150 data were integrated from several series of exposure frames (0.3°
151 width) covering the sphere of reciprocal space.⁴⁹ Absorption
152 correction was applied using the program SADABS.⁵⁰ The data
153 collection for 4 and 5 was performed at the X-ray diffraction beamline
154 (XRD1) of the Elettra Synchrotron, Trieste (Italy).⁵¹ Data sets were
155 collected at 100 K through the rotating crystal method. Completeness
156 was obtained by merging two different data collections done on the
157 same crystal, mounted with different orientations. Data were acquired
158 using a monochromatic wavelength of 0.700 Å on a Pilatus 2M hybrid-
159 pixel area detector. The diffraction data were indexed and integrated
160 using XDS.⁵² Scaling was done using CCP4-Aimless code.^{53,54} The
161 structures were solved by the dual space algorithm implemented in the
162 SHELXT code.⁵⁵ Fourier analysis and refinement were performed by
163 the full-matrix least-squares method based on F2 implemented in
164 SHELXL-2014.⁵⁶ Graphical material was prepared with the Mercury
165 3.9 program.⁵⁷
166

167 ■ RESULTS AND DISCUSSION

168 Single crystal X-ray structures were determined for compounds
169 1–6. In all systems, there can be identified three components,
170 namely, organo-cation, organo-anion, and water/solvent
171 molecules. The invariant feature of the organo-anion is the
172 presence of four sulfonate groups that in TFMS and TFAS are
173 oriented along the vertices of a tetrahedron, whereas in CXS
174 they are oriented on the same side of the calixarene platform
175 (Scheme 2). The sulfonate groups are expected to act as HB
176 acceptors. As far as the organo-cations are concerned, the
177 doubly charged PAM and BPAM exhibit the same number of
178 HB donor groups (four NH₂ moieties), and their main
179 difference derives from the additional torsional degree of
180 freedom imparted by the biphenyl system in BPAM with
181 respect to PAM. The smaller organo-cation of the series is GN,
182 which exhibits three NH₂ groups arranged in a regular trigonal
183 planar geometry bearing a single positive charge. The nature of
184 the cation implies that six to eight HBs can be formed for GN
185 and PAM/BPAM, respectively. In addition, the different
186 symmetry of GN with respect to PAM/BPAM implies a
187 different directionality of the HBs formed by these two groups
188

Scheme 2. (A) Geometrical Representation of the Cationic Components and (B) Full Interaction Maps⁵⁹ (the Interaction Experienced by HB Donors Is Depicted in Red). (C) Anionic Components and (D) Their Full Interaction Maps (the Interaction Experienced by HB Acceptors Is Depicted in Blue)

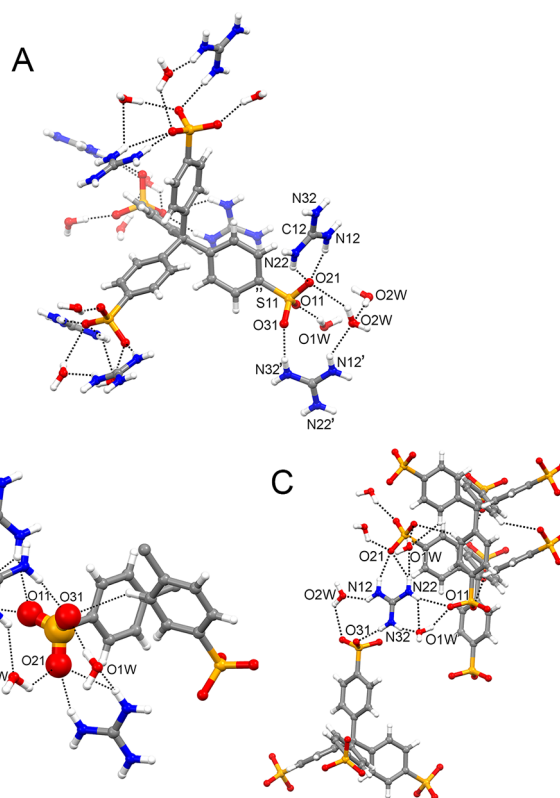
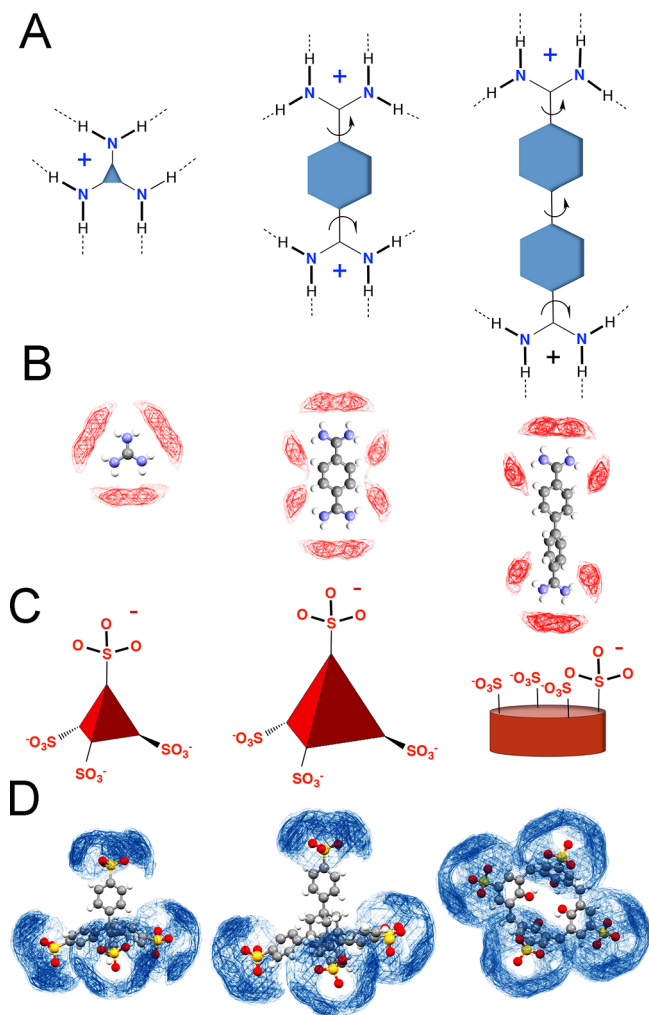


Figure 1. Molecular structure of **1**. The interactions exchanged by TFMS (A and B) and of GN (C). Symmetry codes: ' = $5/4 - y$; $x - 1/4$; $z - 1/4$, '' = $5/4 - y$; $x - 1/4$; $3/4 + z$.

one guanidinium cation, and two water molecules (O1w and 209 O2w). Overall, the structural arrangement consists of four 210 symmetry related GN interacting with a tetra-negatively 211 charged TFMS and eight water molecules $(GN)_4(TFMS) \cdot$ 212 $8H_2O$. The three structural components, namely, cation 213 and water molecules, interact extensively by means of HBs. 214 Each oxygen atom of the SO_3^- group acts as an HB acceptor 215 with water molecules and with the NHs of GN. The 216 guanidinium cation acts as an HB donor with all its six 217 hydrogen atoms (Figure 1C). It interacts with three oxygens of 218 three symmetry related anions, and with three water molecules. 219 The O2w molecule occupies a channel-like cavity, which is 220 parallel to the c crystallographic axis, whereas O1w occupies 221 one portion of space surrounded by cations and anions. The 222 GN, TFMS, and H_2O ratio was also assessed by means of 1H 223 NMR on a sample of crystalline **1** dissolved in deuterated 224 dimethyl sulfoxide (Supporting Information). 225

The stoichiometry of **2** comprises half TFMS moieties, a 226 BPAM cation, and 6.5 water molecules of crystallization, 227 $(BPAM)_2(TFMS) \cdot 13H_2O$. The BPAM cation exchanges 228 several interactions with the surrounding anions and solvent 229 molecules (Figure 2). The BPAM cation bridges the TFMS 230 moieties by forming HBs with the sulfonate groups. Two NH_2 231 fragments on the opposite side of the BPAM unit form HBs, 232 water molecules being located in channel-like cavities. 233 According to the 1H NMR spectrum recorded on a crystalline 234 sample of **2**, the anion/cation/water ratio is approximately 1/2/ 235 9, whereas the structural refinement identified 13 water 236 molecules in the channel-like cavities. 237

The crystal packing of compounds **1** and **2** shows interesting 238 similarities (Figure 3). In fact, the three different architectural 239

188 of cations, Scheme 2. In principle, there are nine potential 189 structural outcomes when combining three cationic and three 190 anionic components. Unfortunately, we could not recover 191 suitable crystals from the TFMS/PAM and TFAS/GN 192 mixtures; instead, the CXS/GN system has already been 193 reported.⁵⁸

194 As mentioned above, a third component was present in all 195 the investigated systems, namely, water molecules or, to a 196 minor extent, methanol molecules. Hence, besides the charge- 197 assisted HBs detected for the cation and anion counterparts, 198 HBs between the organic moieties and water molecules were 199 observed. Not only was a large content of water found in the 200 channels or pores of the structures, but it was found that water 201 molecules were often active components in the construction of 202 the supramolecular assembly bridging between organo-cation 203 and organo-anions.

204 In compounds **1** and **2** tetrahedral TFMS was combined with 205 two different organo-cations: GN and BPAM, Figures 1 and 2. 206 Compounds **1** and **2** crystallize in the tetragonal space group 207 $I4_1/a$ and in the monoclinic space group $C2/c$, respectively. 208 The asymmetric unit of **1** consists of one phenyl- SO_3^- group,

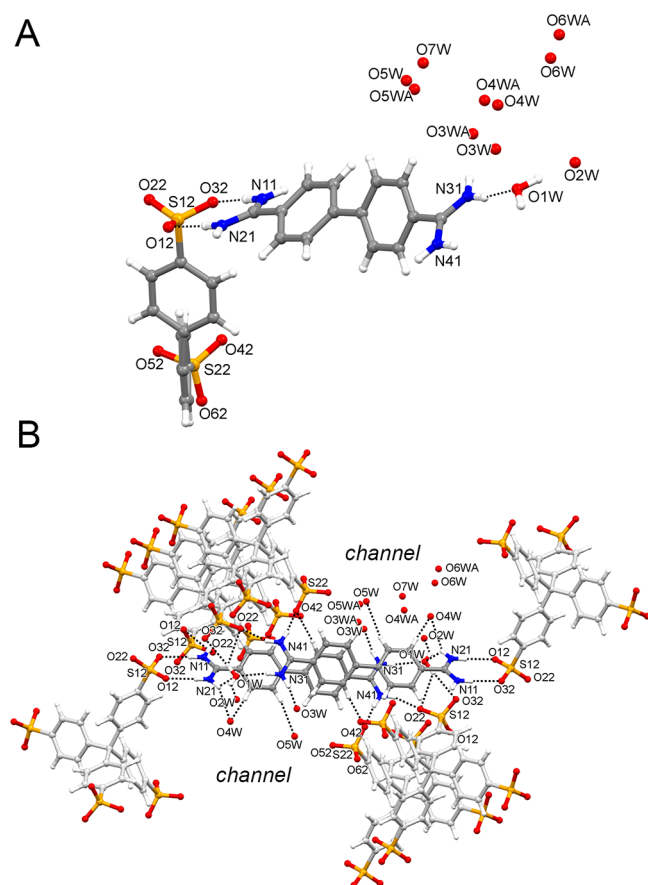


Figure 2. Molecular structure of **2**. (A) Asymmetric unit. (B) Highlight of the interactions exchanged by the BPAM cations.

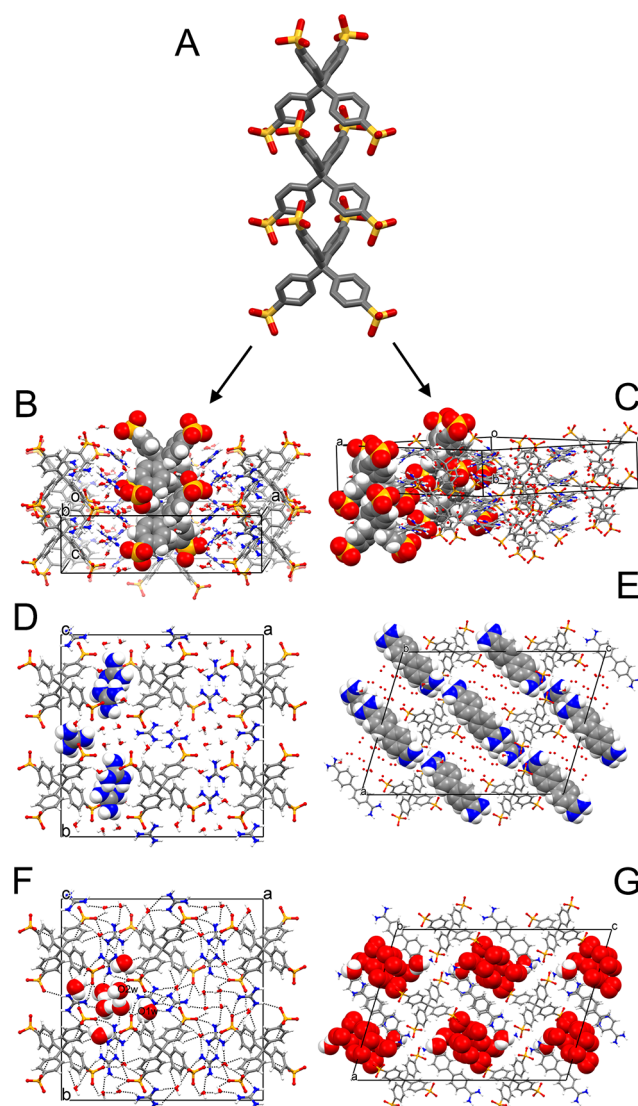


Figure 3. (A) Crystal packing of TFMS in **1** and **2**. Crystal packing of **1** (B, D, and F) and **2** (C, E, and G). Three compartments can be ideally identified in the lattice: one corresponds to the pillars formed by stacked TFMS anions (A–C), the second corresponds to the partially overlaid GN (D) and BPAM (E) cations, while the third is associated with the water molecules located in the channel-like cavity (F and G).

240 components, namely, the sulfonated anions, the organo-cations,
241 and solvent molecules, are approximately arranged in pillars.
242 The TFMS anions are interlocked with the aromatic rings
243 (Figure 3A), whereas the GN or BPAM cations form π – π
244 stacks, which are more regular for BPAM according to the
245 presence of aromatic rings. Additionally, the solvent molecules
246 are located in channels defined by the two charged
247 components.

248 Modification of the central tetrahedral carbon atom with an
249 adamantane moiety resulted in new compounds. In fact, by
250 cocrystallizing TFAS with the organo-cations PAM and BPAM
251 two compounds were obtained: (PAM)₂(TFAS)·9H₂O (**3**) and
252 (BPAM)₂(TFAS)·6.4H₂O·3.6MeOH (**4**), Figures 4 and 5. The
253 compounds **3** and **4** crystallize in the tetragonal space group
254 $P4_2/n$ and in the triclinic $P\bar{1}$, respectively. For both compounds,
255 the TFAS/cation stoichiometry of 1/2 was confirmed by ¹H
256 NMR (see Supporting Information). In the case of **3**, the water
257 content was in agreement with NMR results (nine molecules
258 per anionic unit), while in **4** the ¹H NMR experiments
259 indicated the presence of six water molecules and two methanol
260 molecules, which are slightly fewer than those found by the
261 structural analysis. The asymmetric unit of **3** comprises one Ph-
262 SO₃[−] group of TFAS, one-half PAM cation, and 2.25 water
263 molecules. Each oxygen atom of the SO₃[−] group acts as an HB
264 acceptor: two oxygen atoms are directly linked to PAM cations,
265 whereas the third oxygen atom interacts with symmetry related
266 water molecules (O1w), Figure 4A. PAM acts as an HB donor
267 with all its eight hydrogen atoms interacting with four
268 symmetry related O1w water molecules and with four water

molecules present in the lattice channels (O2w and O4w)
269 (Figure 4B). O1w and PAM form a stack that runs parallel to
270 the *c* axis (see Figure 6C below).
271

The molecular structure of **4** is inherently less symmetric
272 than that of **3** since the compound crystallizes in the triclinic
273 space group $P\bar{1}$. The asymmetric unit comprises a TFMS anion,
274 two BPAM cations, and water/methanol solvent of crystal-
275 lization, Figure 5. The anions do not form pillars as in **1**–**3**, but
276 they form an interlocked dimer, which is surrounded by cations
277 and solvent molecules, see Figure 5B. In this dimer, the two
278 anions are approaching each other with the trigonal face, hence
279 pointing two different –Ph-SO₃[−] groups in opposite directions.
280 This arrangement is different from the one found in **1**–**3**,
281 where the anions are piled along the binary axis of the tetra-
282 hederon.
283

Anionic dimer interactions take place by means of HBs
284 mediated by solvent molecules to form a supramolecular pillar
285

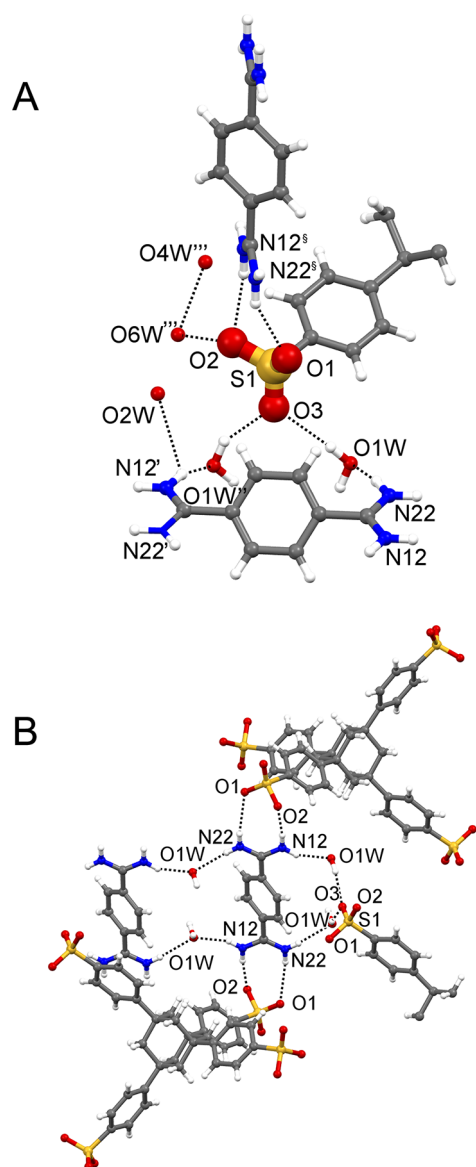


Figure 4. Molecular structure of **3**. (A) Highlight of the interactions exchanged by the sulfonate group with the surrounding cations and water molecules. (B) Interactions exchanged by the PAM cation. Symmetry codes: $' = 1 - x; 1 - y; 2 - z$, $'' = 1 - x; 1 - y; 1 - z$, $''' = 1 - y; 1/2 + x; z - 1/2$, $§ = y; 3/2 - x; 3/2 - z$.

286 that runs parallel to the *a* crystallographic axis (Figure 6B). Also
 287 the BPAM cations form dimers by means of a partial π stack
 288 that involves one of the two phenyl residues (Figure 5A). The
 289 BPAM dimers surround the anionic supramolecular chain, thus
 290 delimiting a channel occupied by solvent molecules that runs
 291 parallel to the [111] direction (Figure 6F). Interestingly, the
 292 crystal packing of **3** reveals considerable similarities to that of **1**
 293 and **2**. In fact, though the TFAS anions are larger than TFMS
 294 (in line with the presence of the adamantane unit instead of a
 295 single carbon atom), they are, like TFMS, interlocked, forming
 296 anionic pillars. The PAM cations alternate with water molecules
 297 (O1w) to form columnar stacks. Each cation exchanges four
 298 HBs with symmetry related O1w within the pillar, whereas in
 299 the direction perpendicular to the pillar axes, it interacts with
 300 two distinct sulfonate groups (Figure 6C).

301 The molecular structures of CXS and GN are reported in the
 302 literature.⁵⁸ For comparison purposes we report the structure of

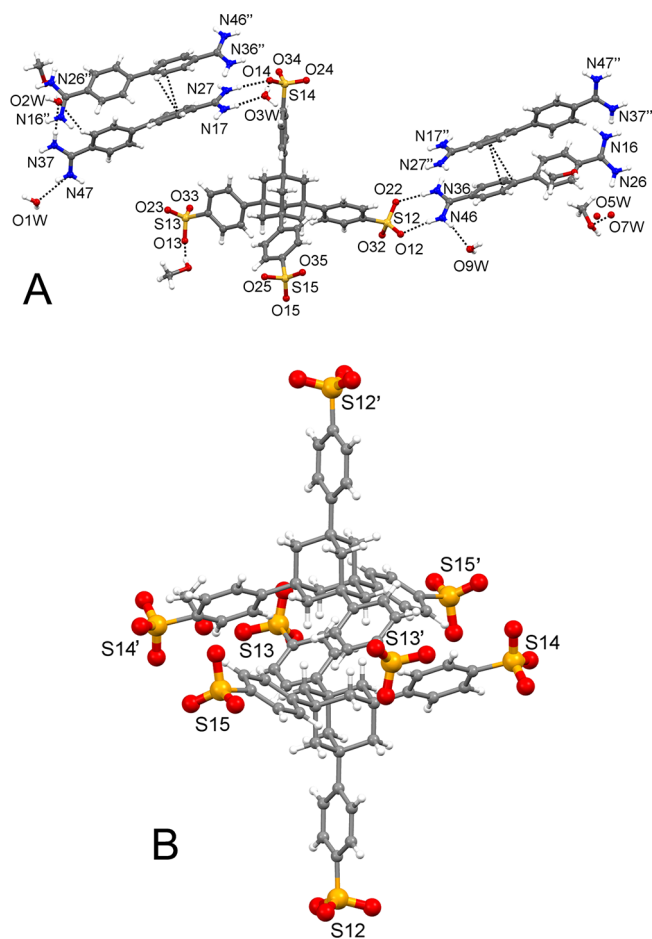


Figure 5. (A) Molecular structure of **4** and (B) the anionic dimer. Symmetry codes: $' = -x; -y; -z$, $'' = -x; 1 - y; 1 - z$.

(GN)₄CXS·3H₂O, which is the system that contains only water
 303 as the crystallization solvent. The asymmetric unit comprises a
 304 CXS anion, and four GN cations and three water molecules
 305 (Figure 7). The crystal packing shows the presence of puckered
 306 layers of GN cations (Figure 7B). Of the three water molecules of
 307 crystallization, one is located inside the CXS cavity, whereas the
 308 remaining two serve as connectors between the CXS and GN
 309 components.
 310
 311

Let us now focus on the CXS/PAM (**5**) and CXS/BPAM
 312 systems (**6**). The asymmetric unit of **5** comprises one CXS
 313 moiety, a PAM cation, two half PAM cations, four water
 314 molecules, and half a methanol molecule of crystallization,
 315 giving rise to the molecular structure (PAM)₂CXS·4H₂O·1/
 316 2MeOH. The ¹H NMR confirmed the 1/2 anion/cation ratio
 317 and the presence of methanol, even though the methanol
 318 quantification was hampered by the presence of peaks partially
 319 overlapping those of the water molecules. All of the sulfonate
 320 groups act as HB acceptors toward -NH₂ groups of PAM and
 321 water molecules. One PAM cation is located above the calix
 322 cavity, exchanging four direct HB interactions with the
 323 sulfonate oxygens surrounding the cavity, a HB with a sulfonate
 324 group of an adjacent calixarene, and three HBs with water
 325 molecules acting as bridges with vicinal anions and cations
 326 (Figure 8A).
 327 f8

The CXS upper rim unit is surrounded by six-symmetry
 328 related PAM cations that interact with the sulfonates by means
 329 of HBs. The PAM cations located outside the CXS upper rim
 330

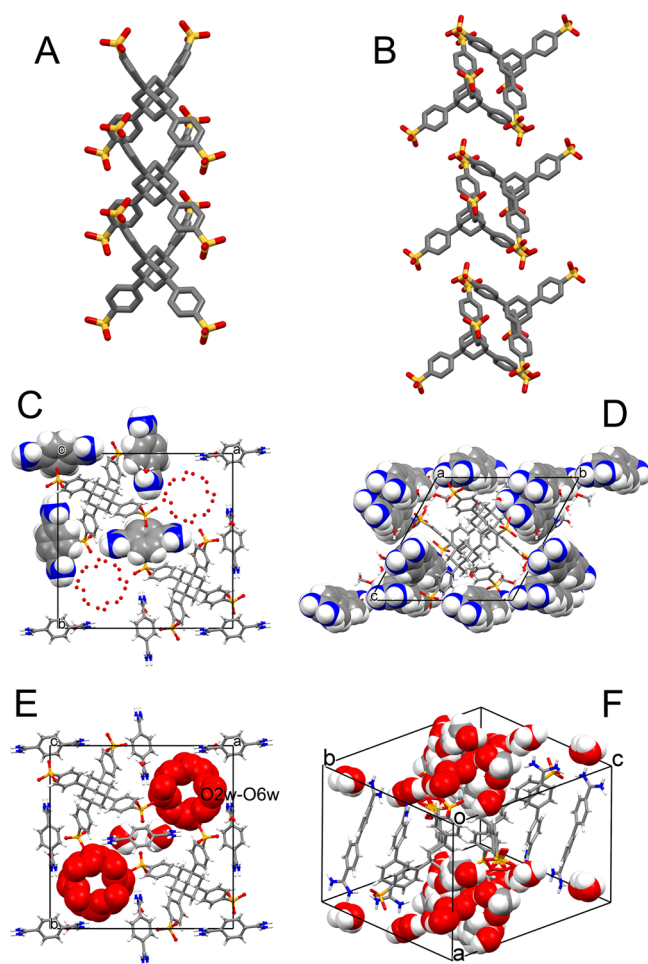


Figure 6. Crystal packing of **3** and **4**. (A) Pillars formed by stacked TFMS anions in **3**. (B) Pillars formed by stacked TFMS dimers in **4**. (C) PAM-water stacks in **3**, (D) BPAM dimers in **4**. Channels occupied by water molecules in **3** (E) and in **4** (F).

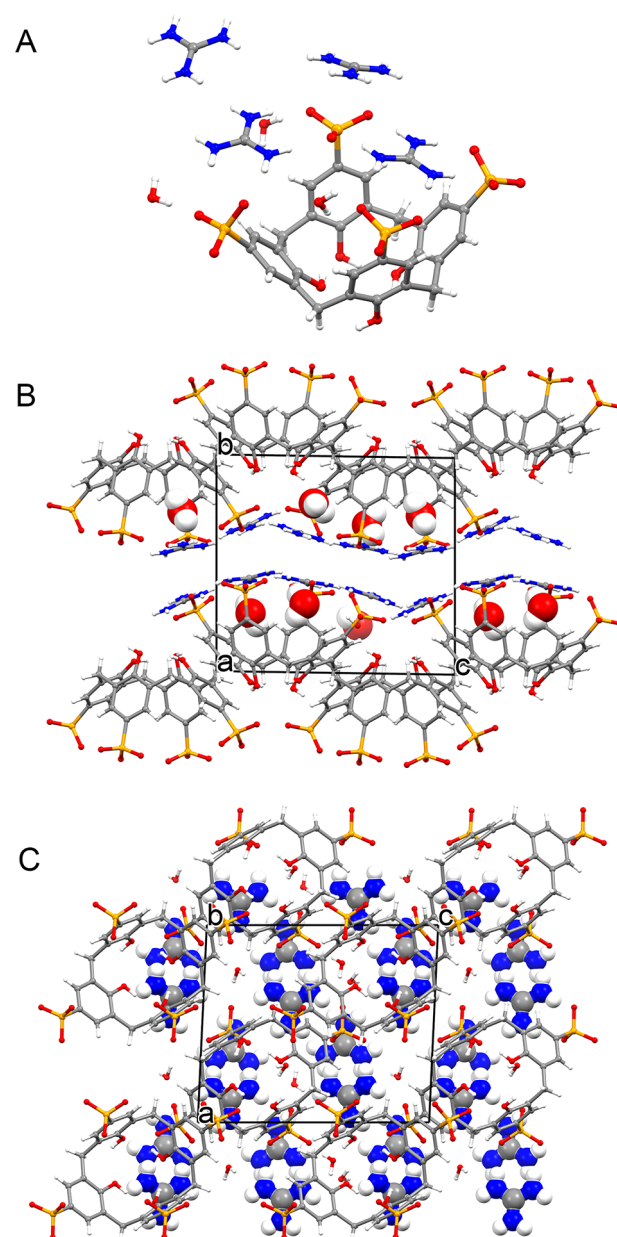


Figure 7. Molecular structure of $(\text{GN})_4\text{CXS}\cdot 3\text{H}_2\text{O}$. (A) Asymmetric unit, (B) crystal packing projected along the a axis, (C) crystal packing projected along the b axis.⁵⁸

link vicinal CSX moieties, favoring the formation of puckered cationic/anionic layers (Figure 8B–C and Figure 9A–B). Within these ideal layers, the CXS anions are oriented in opposite directions (Figure 8C). The water molecules of crystallization occupy channels delimited by SO_3^- and phenyl rings of CXS and by NH_2 moieties of PAM. These channels run parallel to the b crystallographic axis (Figure 9C).

The molecular structure of **6** is reported in Figure 10. The asymmetric unit comprises half a calixarene moiety, one BPAM cation, two half methanol molecules, and four water molecules of crystallization: the overall formula unit corresponds to $(\text{BPAM})_2(\text{CXS})\cdot 8\text{H}_2\text{O}\cdot 2\text{CH}_3\text{OH}$. One methanol molecule is located in the CXS cavity, exchanging $\text{CH}\cdots\pi$ interactions with the methyl group and the phenyl rings surrounding the cavity. The hydroxyl group acts as HB donor with the O(41) atom of a sulfonate residue. Given the CXS symmetry, the methanol molecule is statically disordered in two positions related by a binary crystallographic axis.

The upper rim of the CXS moiety interacts with BPAM cations and water molecules (O1w, O2w, and O3w) through an extensive net of HBs, whereas a water molecule of crystallization (O4w) and a methanol molecule are located close to the lower rim. The aromatic sides of the CXS are involved in two different interactions with the surrounding molecules. The π – π interactions determine the formation of

supramolecular chains that run parallel to the c crystallographic axis (the distance between the aromatic planes is approximately 3.55 Å). Within these chains, the CXS moieties are oriented in opposite fashion (Figure 10D). Likewise, the BPAM cations form irregular stacks parallel to the c axis that are interposed between the CXS chains. As a result, CSX/BPAM mixed supramolecular layers are formed, which are parallel to the ac crystallographic plane. The water molecules are located between these layers acting as HB linkers (Figure 10C).

Hydration Analysis. A common feature of all the supramolecular architectures here reported is the double role played by the water molecules: one fraction acts directly to form HB bridges between the anions and cations, while the other lies in the channels (1–4) or in the more confined cavities (5 and 6). In compound **1** the volume occupied by 370 water molecule was calculated to be 14% of the unit cell 371

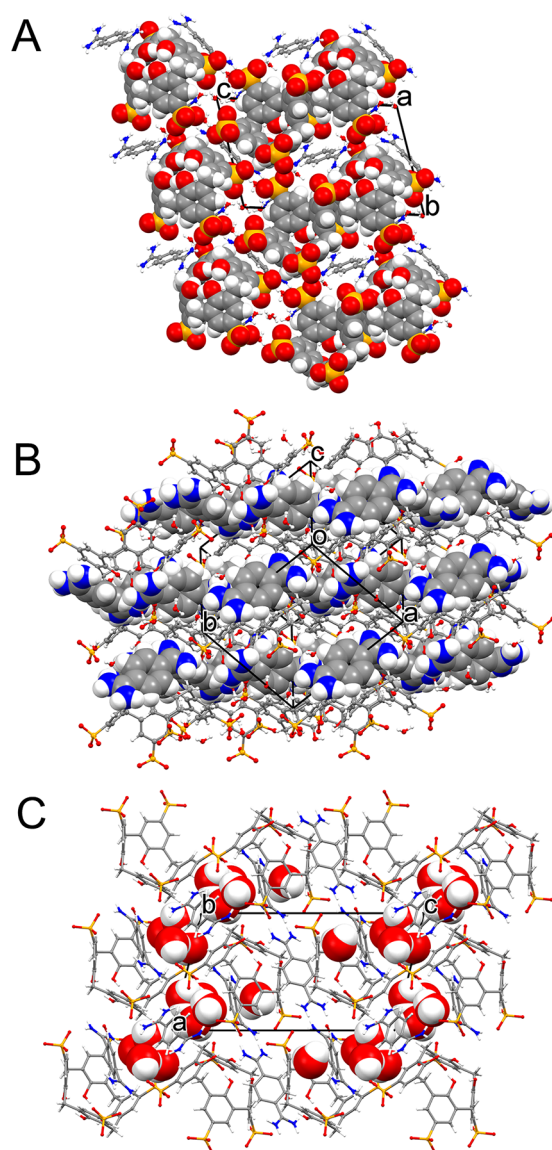


Figure 9. Crystal packing of **5**: CXS anions (A), PAM cations (B), and channels occupied by water molecules (C).

414 tendency to form interlocked columnar molecular arrange-
 415 ments, which are more apt to give rise to channel-like cavities.
 416 In fact, in **5** and **6** the solvent molecules are located in more
 417 defined cavities (as in **5**) or in layers (as in **6**). The DSC
 418 analysis of **5** shows a broad peak at 65 °C, which can be
 419 associated with the loss of the methanol, as observed by X-ray
 420 and NMR analyses. The peaks at 102 °C presumably
 421 correspond to water molecules, which are bound to the
 422 cation–anion framework and H-bonded to other water
 423 molecules. Instead, for compound **6**, the broad peak centered
 424 at about 76 °C may correspond to the methanol molecules
 425 present in the CXS cavity and close to the CXS lower rim, as
 426 well as to the loosely bound water molecules lodged in the
 427 layers of the molecular building.

428 ■ CONCLUSIONS

429 The construction of crystal lattices by tetrafunctional anions,
 430 that protrude in 3D in different directions and mono- or
 431 divalent organic cations, leads to intriguing architectures. In
 432 such structures, the role played by water confirms the tendency

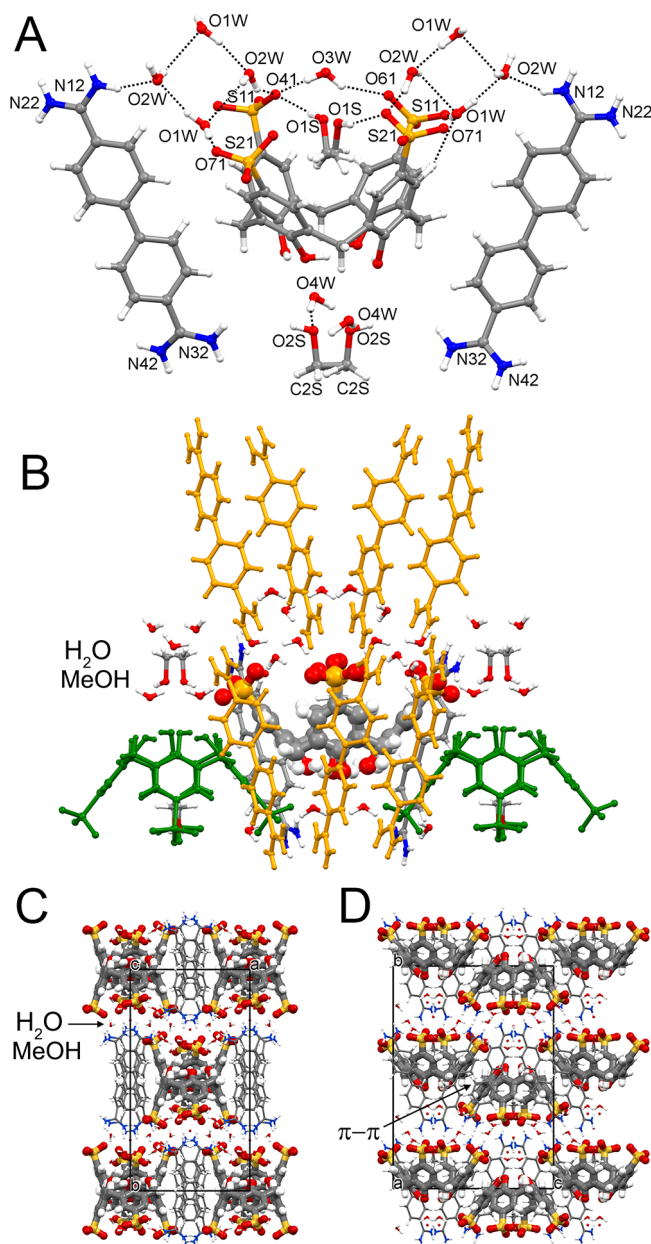


Figure 10. Molecular structure of **6**: (A) network of the HBs exchanged by the cations, anions and solvent molecules. (B) Lattice environment surrounding a CXS unit: the symmetry-related CXS and BPAM cations are depicted in green and orange, respectively. Symmetry codes are not indicated for clarity. Crystal packing of **6**: solvent molecules are located between cation/anion layers (C); highlight of the π - π stack between symmetry related CXS (D).

of multicharged or polar molecules to associate as hydrates.³⁷ 433
 Indeed, water plays a double role in the lattices: (1) it acts as a 434
 strut itself and (2) behaves as a guest in structural channels/ 435
 cavities. The relevant role assumed by water, which in many 436
 cases is elusive to structural characterization, was successfully 437
 identified by single-crystal XRD analysis. The description of 438
 complex structures among densely charged organic molecules 439
 and the interplay of “pronubial” small molecules of water is 440
 relevant to the construction of new hydrates with enhanced 441
 solubility and the perspective to build cocrystals. The high 442
 number of charges and their directional distribution over the 443
 molecular surface result in new properties and enhance the 444

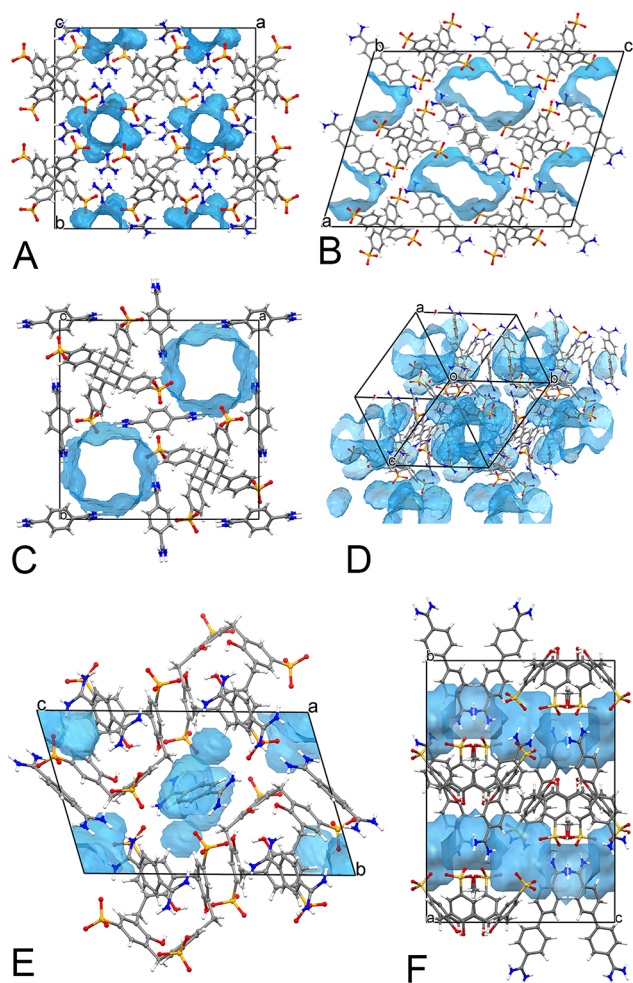


Figure 11. Crystal packing of 1 (A), 2 (B), 3 (C), 4 (D), 5 (E), and 6 (F) showing the volume occupied by water or solvent molecules.

445 potential of the crystallization processes, which is of great
446 relevance in applicative fields where control over the
447 crystallization process is fundamentally of great importance.

448 ■ ASSOCIATED CONTENT

449 ● Supporting Information

450 The Supporting Information is available free of charge on the
451 ACS Publications website at DOI: 10.1021/acs.cgd.7b01538.

452 DSC and TGA plots, ¹H NMR spectra, FT-IR spectra,
453 crystal data, PXRD spectra (PDF)

454 Accession Codes

455 CCDC 1573468–1573473 contain the supplementary crystal-
456 lographic data for this paper. These data can be obtained free of
457 charge via www.ccdc.cam.ac.uk/data_request/cif, or by email-
458 ing data_request@ccdc.cam.ac.uk, or by contacting The
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