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ARTICLE TYPE

Illuminating host–guest cocrystallization between pyrogallol[4]arenes and the ionic liquid 1-ethyl-3-methylimidazolium ethylsulfate

Drew A. Fowler,[a] Constance R. Pfeiffer,[a] Simon J. Teat,[b] Christine M. Beavers,[b] Gary A. Baker*[a] and Jerry L. Atwood*[a]

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The host–guest complexes of seven unique cocrystals containing pyrogallol[4]arenes and the ionic liquid 1-ethyl-3-methylimidazolium ethylsulfate are fully described. The investigation of these cocrystals is directed at expanding the control of the solid-state structures of these unique host–guest assemblies. The effects of varying conditions such as solvent choice and aliphatic tail length appended on the host macrocycle are explored and shed new light on the resultant supramolecular structures.

Introduction

The macrocycles known as pyrogallol[4]arenes (PgC$_x$), versatile members of the calixarene family, have been steadily gaining attention since the structure of a self-assembled hexameric PgC$_x$ nanocapsule was first reported in 1999.[1] The alkyl functionalised macrocycles typically assume a bowl-shaped conformation in which the upper-rim of the macrocycle is decorated with twelve hydroxyl groups that play an integral role in guiding much of the supramolecular chemistry of these molecules. PgC$_x$s have drawn significant interest due to the self-assembly of the macrocycles into large assemblies including hydrogen-bonded nanocapsules, nanotubes, and metal-organic nanocapsules (MONCs).[1,2] The MONCs are particularly attractive due to the ability to control the formation of hexameric or dimeric capsules via the identity of co-included metal ions or particular synthetic conditions.[3] These capsules reveal a number of interesting properties. For example, the Ga-seamed hexamer, which is only partially seamed, has been shown to allow the transport of ions into the interior of the capsule, ultimately binding them as guests within the bowls of the PgC$_x$ macrocycles.[4] Exploration of the more well-known calixarene and resorcinarene families has continually expanded to hosting ever diverse guests, including fullerenes and ammonium ions.[5] In particular, Raston and co-workers have reported several instances of *p*-sulfonatocalix[4]arenes forming host–guest complexes with imidazolium, pyridinium, and phosphonium cations, all of which are staples in ionic liquid chemistry.[6] This penchant for hosting various species has extended to the pyrogallol[4]arenes which are also capable of forming host–guest assemblies with a wide variety of molecular guests.[7]

Ionic liquids (ILs) are beginning to emerge as novel multifunctional crystallization media, being employed as neutral solvents, structure directing templates, amphiphilic self-assembly media, charge compensating species, and anti-solvents.[8] This rise in interest can be understood by a recognition for the distinctive features they can bring, both in terms of the peculiar physicochemical properties common to iconic ILs—wide thermal operating window of the liquid state, low levels of interfacial tension (yielding high nucleation rates) and, in a vast number of instances, low volatility even under high vacuum—as well as prospects for tailoring the individual ions comprising the IL, offering a level of fine control not otherwise available with traditional crystallization media. The inclusion of transition metal or lanthanide ions is also feasible,[9] permitting the direct integration of functionality (*e.g.,* chirality, magnetism, optical activity, catalytic activity, and luminescence) into the liquid proper. Interestingly, although considered a detriment to many applications, the high viscosity of ILs can actually offer a critical advantage in crystal engineering approaches making use of slow diffusion layering techniques for growing high-quality crystals.[10]

Another outstanding property of ILs is that they are typically more structured in the liquid state relative to conventional organic solvents, exhibiting extended hydrogen-bonding networks reminiscent of the solid state.[11] In fact, ILs can be considered ‘supramolecular polymers’ with a composition described by $\{[C_xA_{x-n}]^{n+}[C_{x-n}A_x]^{n-}\}_m$, with C being the cation (typically, a 1,3-dialkylimidazolium or other onium ion) and A being the anion.[12] This property of supramolecular organization allows ILs to be used as ‘entropic drivers’ during crystallization. Moreover, due to their high thermal stability and low vapour pressure, there is no need to use high-pressure reactors in reactions at temperatures as high as 200 °C or so, giving rise to the field of ionothermal synthesis, a cousin to hydrothermal synthesis wherein water is replaced by IL as the solvent milieu.[13] These strategies have proven very useful for isolating or crystallizing different products from ILs, leading to exciting new prospects for crystal engineering (e.g., polymorph design) and an alluring problem-solving tool in difficult crystallization cases.[14]

Recently, we reported on host–guest assemblies containing PgC$_x$s and two different imidazolium-based ILs.[15,16] The first of these was accomplished through the crystallisation of PgC$_3$ in 1-ethyl-3-methylimidazolium ethylsulfate ([emim][EtSO$_4$]).[15]

Although one of the generally favourable attributes contributing to the popularity of ILs is their low vapour pressure (*vide supra*), this trait makes difficult the use of one of the most common methods for crystallisation, *viz.*: slow evaporation. Thus, a method was developed to adapt to the lower vapour pressure. We summarize here our efforts in this area. Namely, we present single-crystal X-ray diffraction structures of several PgC$_x$ and [emim][EtSO$_4$] cocrystals synthesized in both neat [emim][EtSO$_4$] and various solvents.

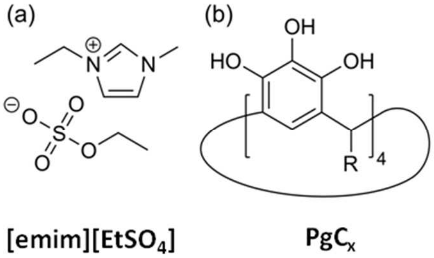

Fig. 3 Chemical structures of (a) 1-ethyl-3-methylimidazolium ethylsulfate and (b) the generic structure of pyrogallol[4]arenes.

Results

Cocrystal 1

Single crystal X-ray diffraction data collected of crystals grown from a neat solution of PgC$_2$Ph and [emim][EtSO$_4$] reveals cocrystal **1** to be a host–guest cocrystal. The asymmetric unit is comprised of a single PgC$_2$Ph macrocycle, three [emim][EtSO$_4$] ion pairs, and three water molecules disordered over five positions. The cocrystal crystallizes in the monoclinic space group P21/n and yields a bilayer-type structure. The host–guest complex is formed by one of the three [emim]$^+$ ions being positioned within the host PgC$_2$Ph bowl. The second [emim]$^+$ resides between the tail groups of the PgC$_2$Ph and the third is positioned between the bilayers (see **Fig. 2**). Each of the [EtSO$_4$]$^-$ ions is participating in hydrogen-bonding around the upper-rims of the macrocycles with the macrocycles and the disordered water molecules.

The guest [emim]$^+$ ion is disordered at the ethyl and methyl groups' positions and the major component is modelled at 70% occupancy and the minor at 30% occupancy. The major component guest [emim]$^+$ ion is complexed in the bowl of the PgC$_2$Ph molecule through six non-covalent interactions (see **Fig. 3**). Three of these interactions are C–H···O hydrogen bonds and three are C–H···π interactions. In all three interactions the hydrogen atom is donated from the [emim]$^+$ ion to phenolic oxygen atoms with two of the three being donated from hydrogen atoms of the imidazolium ring with H···O distances 2.82 and 2.85 Å. The third C–H···O hydrogen bond occurs with a hydrogen atom from the methyl group with a C–H···O distance of 2.98 Å. All three of the C–H···π interactions occur between hydrogen atoms of the ethyl group of the [emim]$^+$ ion and aromatic rings of the host macrocycle. The three H···π centroid distances are 2.76, 2.82, and 2.84 Å. There is also a single C–H···π interaction between the [emim]$^+$ ion that is positioned between the tails of the PgC$_2$Ph. Here, a hydrogen atom of the imidazolium ring is participating in the C–H···π interaction with one phenyl ring of a tail group and has a H···π centroid distance of 2.69 Å. This [emim]$^+$ ion is also donating a hydrogen from the methyl group to a C–H···O hydrogen bond with an upper-rim oxygen atom of a symmetry related PgC$_2$Ph molecule with a H···O distance of 2.61 Å. There is a single C–H···O hydrogen bond between the methyl of the third [emim]$^+$ ion and an upper-rim oxygen atom with a C–H···O distance of 2.72 Å. The interactions of the minor component guest [emim]$^+$ ion only differ by the interactions involving the ethyl and methyl groups. Here, there are also four interactions originating from hydrogen atoms of the ethyl and methyl groups, two from each. The two interactions from the methyl group are C–H···π interactions with H···π aromatic centroid distances of 2.81 and 2.96 Å. The two C–H···O hydrogen bonds occurring with the ethyl group have H···O distances of 2.74 and 2.76 Å.

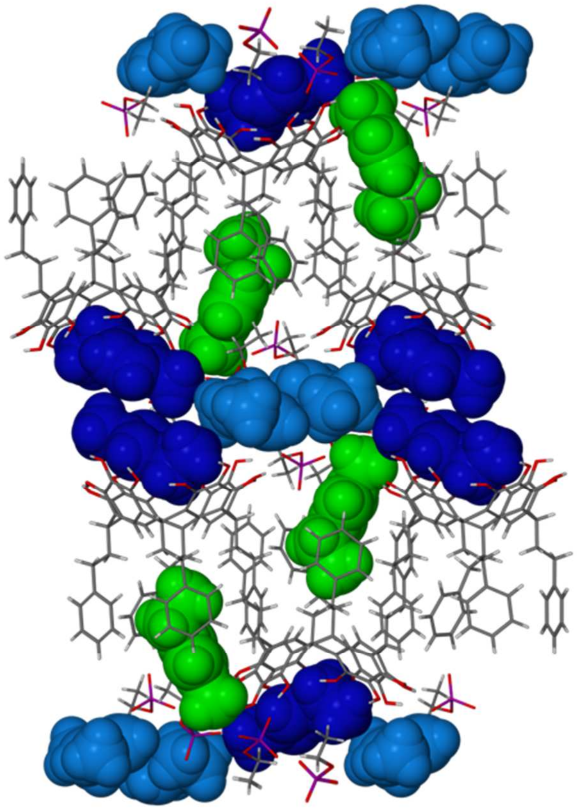

Fig. 2 Packing of cocrystal **1,** PgC$_2$Ph·3{[emim][EtOH]}·3H$_2$O, with the guest [emim]$^+$ ions displayed in space-filling representation and varying colours to display different positions. Dark blue = guest, light blue = between the bilayers' upper-rims, and green = resides in tails.

The twelve upper-rim hydroxyl groups are also participating in extensive hydrogen bonding. Six of these interactions are occurring through the often observed intramolecular hydrogen bonds around the upper-rim of the macrocycle with O···O distance range of 2.68-2.90 Å. Of the remaining hydroxyl groups, four are hydrogen bonding to [EtSO$_4$]$^-$ ions with O···O distances of 2.65, 2.73, 2.84, and 2.94 Å. The last two are hydrogen bonding to disordered water molecules with O···O distances of 2.62 and 2.70 Å. Typically, when pyrogallol[4]arenes crystallize in bilayer structures there is intermolecular hydrogen bonding between neighbouring macrocycles. In this structure, however, there is only a single position where two upper-rim phenols are within close enough proximity to hydrogen bond.

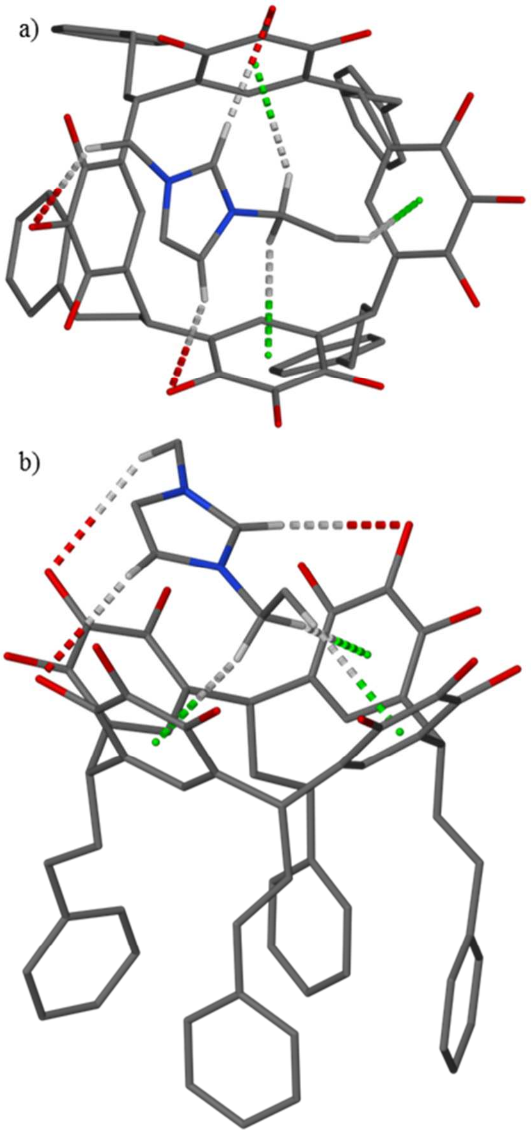

Fig. 3 Alternate views of cocrystal **1,** PgC$_2$Ph·3{[emim][EtOH]}·3H$_2$O, in stick representation illustrating host-guest interactions. Hydrogen atoms not involved in interactions are hidden for clarity.

Cocrystal 2

In cocrystal **2**, as with the remaining cocrystals discussed here, the crystallisation of the host–guest complex has been carried out in a common organic solvent rather than using the IL as the solvent. For cocrystal **2**, the solvent used is acetone. Single crystal X-ray diffraction data revealed a bilayer-type host–guest cocrystal which crystallizes in the monoclinic space group P21/c. The asymmetric unit consists of one half of a PgC$_1$ macrocycle, one half of two [emim]$^+$ ions, a water molecule, half of one acetone molecule, a disordered acetone molecule at partial occupancy, and half of a sulphate ion (the ethyl group has been hydrolysed). The host–guest complexes pack tightly and form overlapping layers yielding cation channels (see **Fig. 4**). The sulphate counter-ions hydrogen-bond to the pyrogallol[4]arenes of opposing layers and adjacent channels. The water molecules are donating hydrogen-bonds to neighbouring sulphate ions and accepting hydrogen-bonds from opposing PgC$_1$ molecules. One of the two acetone molecules is positioned between the four methyl tails of each PgC$_1$. The second molecule of acetone is disordered over two positions between the tails of neighbouring macrocycles. One of the [emim]$^+$ ions is also disordered over two positions between pyrogallol[4]arenes of neighbouring channels while the second is the guest cation.

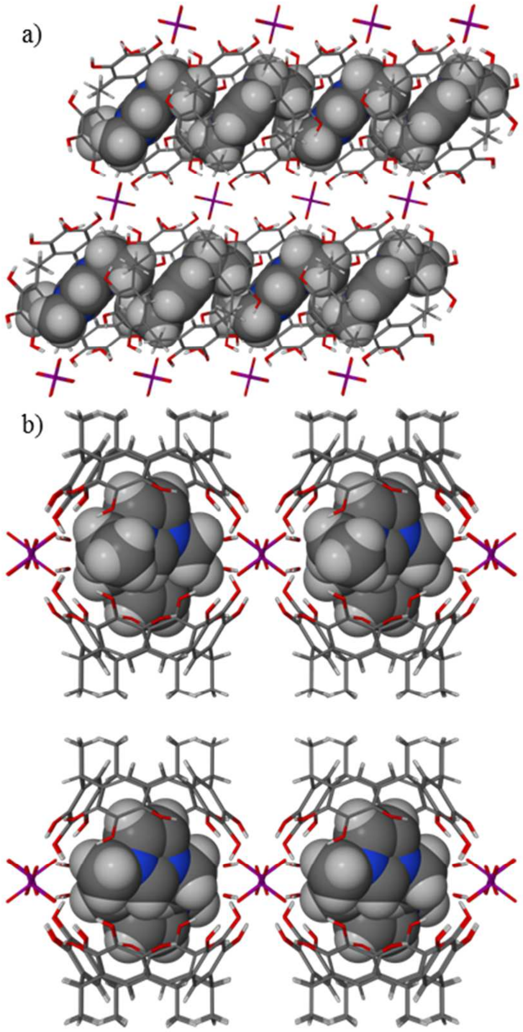

Fig. 4 Views of the packing of cocrystal **2,** 0.5PgC$_1$·1.5[emim]$^+$ ·0.5 [SO$_4$]$^{2-}$·H$_2$O·1.5C$_3$H$_6$O, along the a) *b* axis and b) *c* axis. Guests are displayed in space-filling representation while macrocycles, water molecules, and counter-ions are displayed in stick representation.

The host–guest complex in cocrystal **2** forms through five non-covalent interactions (see **Fig. 5**). Two of these are symmetry equivalent C–H···π interactions where the symmetry equivalent hydrogen atoms of the imidazolium ring are donated to the benzene rings of the macrocycle with a H···π distance of 2.85 Å. The remaining three interactions are C–H···O hydrogen bonds donated from the ethyl and methyl groups of the [emim]$^+$ ion to the upper-rim hydroxyls with H···O distances of 2.63, 2.85, and 2.91 Å.

As previously mentioned, intermolecular hydrogen bonding between molecules of PgC$_1$, water, and sulphate ions provides the support for the bilayers. While each PgC$_1$ has four positions where it could hydrogen bond to neighbouring macrocycles, two to each adjacent macrocycle in the same layer, these upper-rim hydroxyls are instead participating in more favourable hydrogen bonds with water molecules or

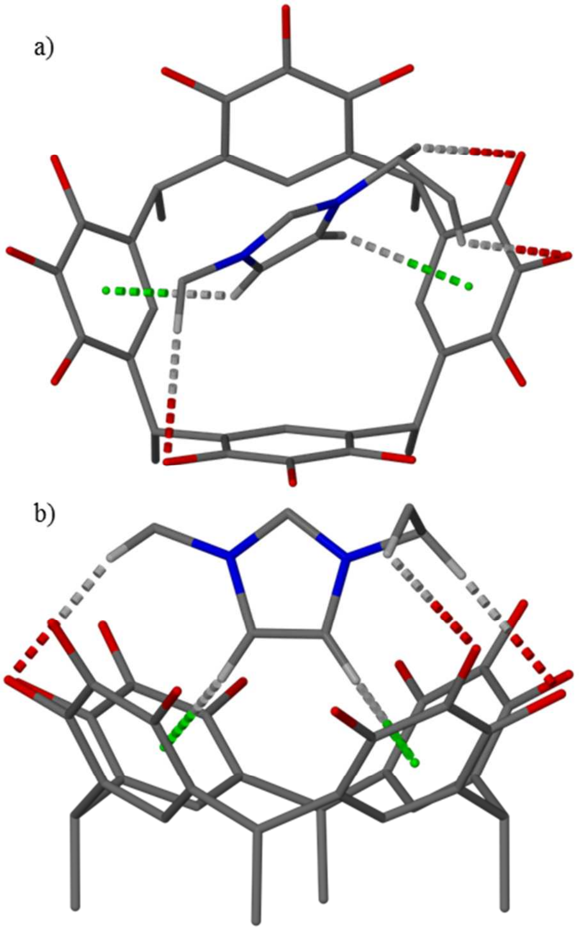

Fig. 5 Alternate views of the host-guest complex in cocrystal **2**, $0.5PgC_1 \cdot 1.5[emim]^+ \cdot 0.5[SO_4]^{2-} \cdot H_2O \cdot 1.5C_3H_6O$, displayed in stick representation illustrating the host-guest interactions as dashed bonds. Hydrogen atoms not involved in interactions are hidden for clarity.

intramolecular hydrogen bonds. The axis of the two-fold rotation runs through the centre of the macrocycle yielding six symmetry-unique hydrogen bonds donated from each macrocyle's upper-rim hydroxyl groups. These include two intramolecular hydrogen bonds with O···O distances of 2.78 and 2.80 Å. Two of the phenolic groups are donating hydrogen bonds to water molecules with O···O distances of 2.73 and 2.79 Å. The last two unique hydrogen bonds donated from the upper-rim phenols are to sulphate ions and have O···O distances of 2.69 and 2.73 Å. Each sulphate ion is therefore accepting four hydrogen bonds from these phenolic groups. Each sulphate ion is also accepting four hydrogen bonds from water molecules two of which are unique and have O···O distances of 2.78 and 2.80 Å

Cocrystal 3

Cocrystal **3**, where PgC_1 and $[emim][EtSO_4]$ were crystallized from a solution of acetonitrile, also forms a bilayer-type structure in the triclinic space group P-1. The asymmetric unit contains one PgC_1, one $[emim][EtSO_4]$ ion pair, one solvent acetonitrile, and a single water disordered over two positions. Here, the bilayer has crystallised such that the host–guest complexes stack in slightly offset pairs (see **Fig. 6**). The two macrocycles that make up these pairs do not hydrogen-bond to one another due to the large distance of separation occurring from the stacking of the host–guest complexes. However, these two macrocycles cooperatively hydrogen-bond to three $[EtSO_4]^-$ ions through six hydrogen bonds donated from upper-rim hydroxyls. Two of the three $[EtSO_4]^-$ ions contain hydrogen bonds which are symmetry related and the two unique hydrogen bonds have O···O distances of 2.74 and 2.85 Å. The two hydrogen that bond to the third $[EtSO_4]^-$ ion have O···O distances of 2.79 and 2.86 Å. Each macrocycle is also hydrogen bonding to a fourth $[EtSO_4]^-$ ion with a O···O distance of 2.66 Å. There is a single hydrogen-bond donated to the disordered water molecule with a O···O distance of 2.79 Å. Of the remaining hydrogen bonds being donated by the upper-rim hydroxyl groups, two are to neighbouring macrocycles, with O···O distances of 2.74 and 2.76 Å, and five are intramolecular hydrogen bonds around the upper-rim with O···O distances in the range 2.71-2.82 Å.

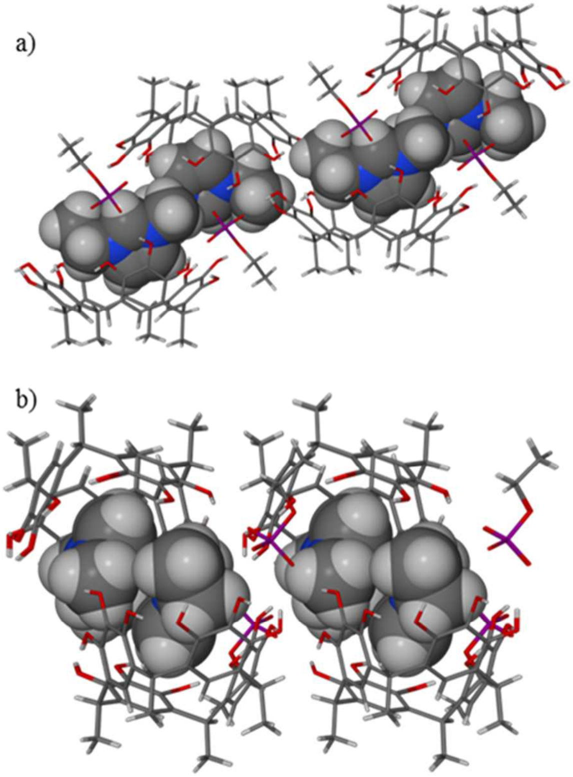

Fig. 6 Views of cocrystal **3,** $PgC_1 \cdot \{[emim][EtSO_4]\} \cdot H_2O \cdot C_2H_3N$, along the a) *a* axis and b) *b* axis. Guests are displayed in space-filling representation while macrocycles and counter-ions are displayed in stick representation.

The guest molecule is disordered over two positions; however, it is only disordered at the positions of the ethyl and methyl groups with the major portion modelled at 80% and the minor at 20%. The host–guest complex with the major position of the guest in cocrystal **3** is formed through six non-covalent interactions, three C–H···π, and three C–H···O (see **Fig. 7**). In two of the C–H···π interactions the hydrogen atoms are donated from the imidazolium ring to the PgC_1 and have C–H···π distances of 2.45 and 2.68 Å. The third C–H···π occurs through the donation of a hydrogen atom of the ethyl group of the $[emim]^+$ ion to the PgC_1 with a C–H···π distance of 2.60 Å. Two of the C–H···O interactions also occur through donation of hydrogen atoms of the ethyl group and one from the methyl group of the $[emim]^+$ ion to the oxygen atoms of the upper-rim hydroxyl groups of the PgC_1

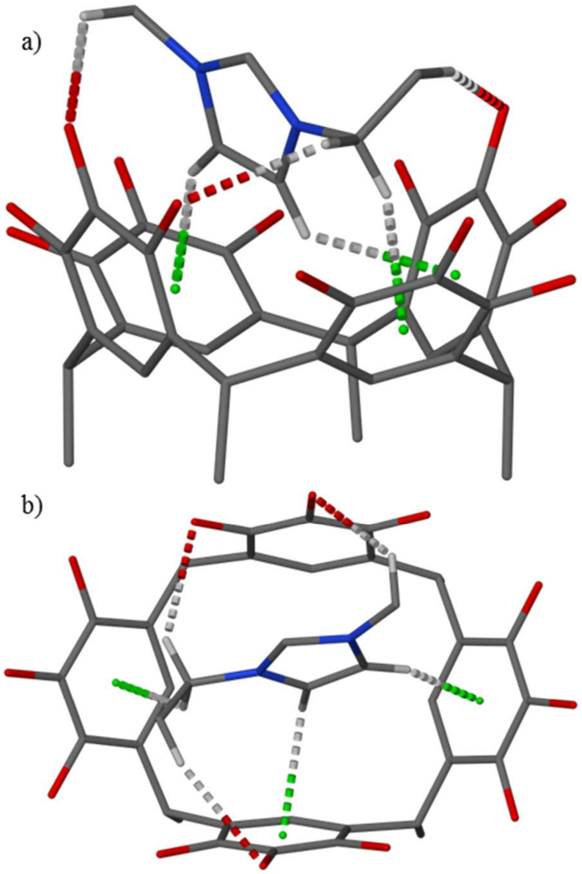

Fig. 7 Alternate views of the host-guest complex in cocrystal **3**, PgC$_1$·{[emim][EtSO$_4$]}·H$_2$O·C$_2$H$_3$N displayed in stick representation illustrating the host-guest interactions as dashed bonds. Hydrogen atoms not involved in interactions are hidden for clarity.

with C–H···O distances of 2.63, 2.72, and 2.73 Å. The interactions of the minor position of the guest only differ by the interactions formed with the ethyl and methyl groups. In this case there are four C–H···O hydrogen bonds, two donated from each the ethyl and methyl groups of the [emim]$^+$ ion. The distances of these interactions are in the range of 2.62-2.90 Å.

Cocrystal 4

In cocrystal **4**, acetone is again the solvent used for crystallisation and PgC$_2$ is the macrocycle used as the host. Similar to **2**, the [EtSO$_4$]$^-$ ion has undergone hydrolysis to a sulphate ion. The asymmetric unit of the cocrystal contains this sulphate ion, two [emim]$^+$ counter ions, two PgC$_2$ molecules, two acetone molecules, and seven water molecules crystallising as a bilayer type structure in the monoclinic space group Cc. The guest in cocrystal **4** is contained by a pair of PgC$_2$ macrocycles in a bilayer-type packing structure (see **Fig. 8**). It should be noted that the guest molecule has been modelled over two positions due to disorder. The major position has been modelled at 70% occupancy and the minor position 30%.

For both guest positions, this dimeric host–guest complex is formed via eight non-covalent interactions between the guest and the two host PgC$_2$ macrocycles. With the host–guest complex formed with the major guest position each macrocycle is accepting four C–H···O or C–H···π interactions from the guest to the upper-rim hydroxyl groups or benzene rings, respectively (see **Fig. 9**). Three of these eight interactions are of the C–H···π type and have C–H···π distances of 2.63, 2.68, and 2.77 Å. The remaining five interactions are C–H···O hydrogen bonds and have C–H···O distances of 2.65, 2.68, 2.77, 2.78, and 2.84 Å. In the host–guest complex formed with the minor guest position there are four C–H···π interactions and four C–H···O hydrogen bonds. The four C–H···π interactions have C–H···π aromatic centroid distances ranging from 2.56-2.89 Å. The four C–H···O interactions have C–H···O distances in the range of 2.68-2.93 Å.

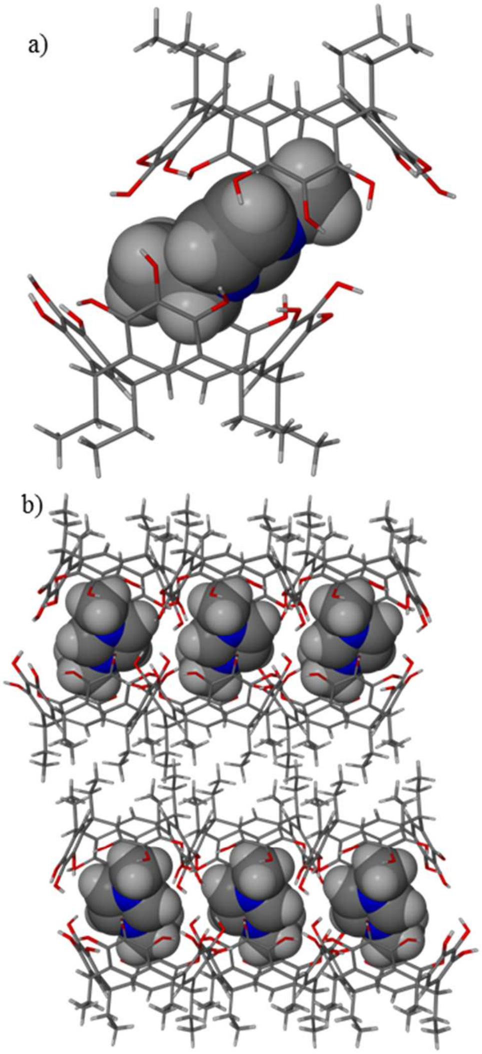

Fig. 8 a) A single dimeric host-guest complex found in cocrystal **4**, 2PgC$_2$·2[emim]$^+$·[SO$_4$]$^{2-}$·7H$_2$O·2C$_2$H$_6$O. b) Packing of cocrystal **4** viewed along the *a* axis. The guests are displayed in space-filling representation while macrocycles are displayed in stick representation.

The two PgC$_2$ molecules that each dimeric complex is constructed of do not form direct hydrogen bonds to one another but rather hydrogen bond through the disordered water molecules and sulphate ions. There are two sulphate ions accepting hydrogen bonds from the macrocycles. One macrocycle is donating three hydrogen bonds to the two sulphate ions with O···O distances of 2.68, 2.83, and 2.87 Å. The second macrocycle is donating two hydrogen bonds to the same two sulphate ions with O···O distances of 2.72 and 2.73 Å. There are also two water molecules that are accepting a single hydrogen bond from each macrocycle. The O···O distances of the two hydrogen bonds to

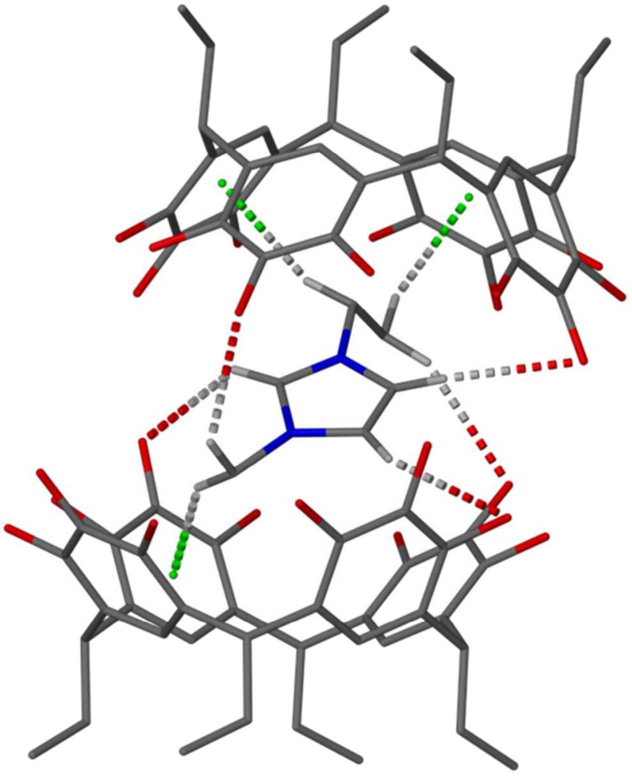

Fig. 9 Stick representation of a dimeric host-guest complex formed in cocrystal **4**, $2PgC_2{\cdot}2[emim]^+{\cdot}[SO_4]^{2-}{\cdot}7H_2O{\cdot}2C_2H_6O$, with the observed non-covalent interactions shown as dashed bonds. Hydrogen atoms not involved in interactions have been hidden for clarity.

the first water molecule are 2.60 and 2.69 Å. The two hydrogen bonds of the second water molecule have O···O distances of 2.77 and 2.61 Å. The two macrocycles are also hydrogen bonding to four other water molecules through a total of five hydrogen bonds. In each of these cases the water molecules are accepting hydrogen bonds from a single PgC_2. The O···O distances for these hydrogen bonds are 2.63, 2.78, 2.63, 2.73, and 3.02 Å. The remaining upper-rim hydroxyls, five for each PgC_2, are donating hydrogen bonds to other upper-rim hydroxyl groups. In both cases one is to a PgC_2 of a neighbouring dimer and the rest are intramolecular hydrogen bonds. The O···O distances of these hydrogen bonds are in the range of 2.62-2.75 Å.

Cocrystal 5

For cocrystal **5** the solvent and macrocycle used is acetonitrile and PgC_2, respectively. Unlike cocrystals **2** and **4** where the acetone cocrystals of PgC_1 and PgC_2 with [emim][$EtSO_4$] have quite different structures, the structures using these same macrocycles with acetonitrile are quite similar. The unit cell parameters are very close with only a slight lengthening along the *a* and *b* axes accompanied by a small change in the β angle. The contents of the unit cell are also the same, with the macrocycle in **5** being PgC_2 respectively (see **Fig. 10**).

In **5** the six non-covalent host–guest interactions consists of three C–H···π and three C–H···O interactions. The one interaction which does not correlate directly to the host–guest interactions seen in **3** is a C–H···O interaction. It is simply closer to a different oxygen atom on the same relative pyrogallol moiety with a C–H···O distance of 2.84 Å. The other two C–H···O

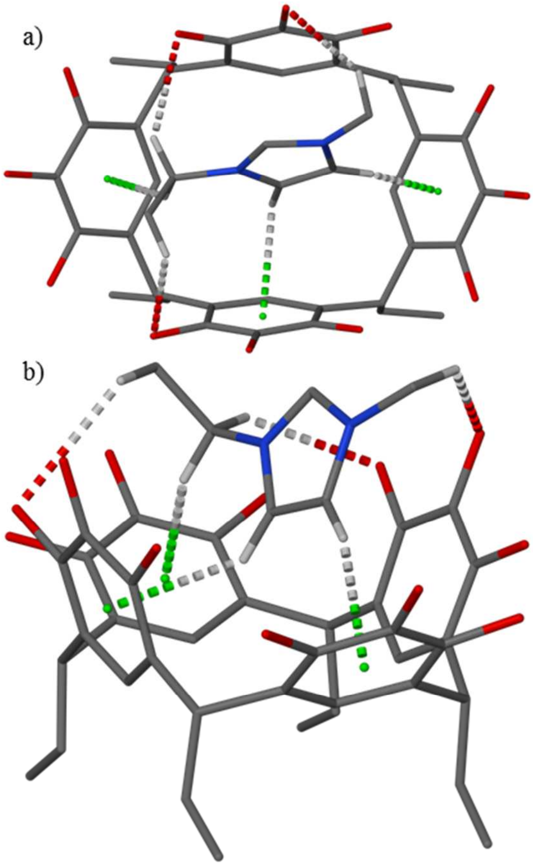

Fig. 10 Alternate views of the host-guest complex found in cocrystal **5,** $PgC_2{\cdot}$ {[emim][$EtSO_4$]}$\cdot H_2O{\cdot}C_2H_3N$, displayed in stick representation illustrating the host-guest interactions as dashed bonds. Hydrogen atoms not involved in interactions are hidden for clarity.

hydrogen bonds have C–H···O distances of 2.63 and 2.80 Å. The three C–H···π interactions have C–H···π aromatic centroid distances of 2.43, 2.56, and 2.61 Å.

As expected, due to the isostructural nature of **5** compared to **3**, the stacking of the bilayer is again as offset dimers (see **Fig. 11**), which results in a very similar hydrogen bonding network. There are again five unique intramolecular hydrogen bonds around the upper-rim of each macrocycle. The O···O distances are in the range of 2.70-2.90 Å. Also, similar to **3** there are two unique hydrogen bonds with adjacent macrocycles and one with the disordered water molecule which have O···O distances of 2.84, 2.88 and 2.80 Å, respectively. There are four unique hydrogen bonds being donated to $[EtSO_4]^-$ ions. Also similar to **3** two of these $[EtSO_4]^-$ ions are cooperatively hydrogen bonding to the pair of PgC_2 macrocycles which make up the offset dimers. Here these two unique hydrogen bonds have O···O distances of 2.80 and 2.93 Å. The remaining two hydrogen bonds have O···O distances of 2.74 and 2.90 Å.

Cocrystal 6

Cocrystal **6** is the third cocrystal formed from a solution of acetone and as in both other cocrystals discussed here, **2** and **4**, the presence of a sulphate ion in the crystal structure reveals that the $[EtSO_4]^-$ ion has undergone hydrolysis. The asymmetric unit also contains a single macrocycle, PgC_4, a guest $[emim]^+$ ion, and two water molecules crystallised in the triclinic space group P-1.

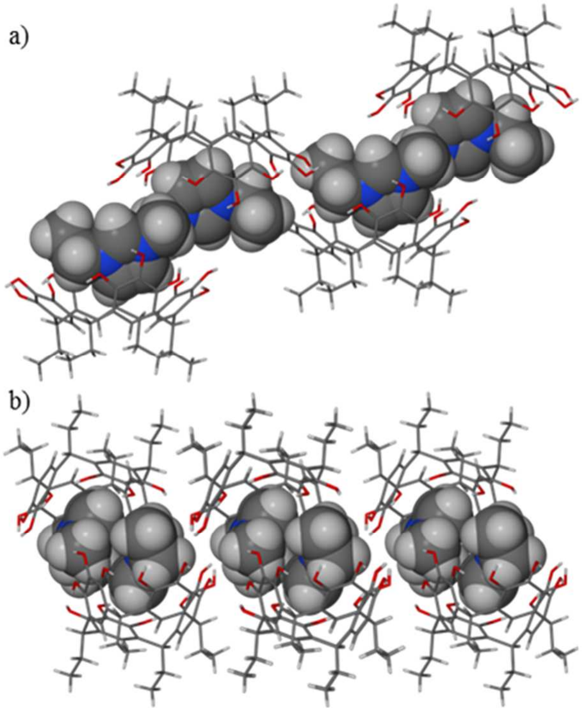

Fig. 11 Views of the packing of cocrystal **5**, PgC_2· {[emim][$EtSO_4$]}·H_2O·C_2H_3N, along the a) *a* axis and b) *c* axis. Guests are displayed in space filling representation while macrocycles and counter ions are displayed in stick representation.

Unlike **2** and **4** there is only a single guest $[emim]^+$ counter ion to balance the charge of the hydrolysed $[EtSO_4]^-$ ion. This is likely due to the $[SO_4]^{2-}$ ion being protonated, yielding a $[HSO_4]^-$ ion, correlating to the crystal data. The quality of the data enabled us to determine the location of this hydrogen atom establishing the charge balance of the structure. Furthermore the hydrogen is donated in a hydrogen bond to one of the two water molecules with a O···O distance of 2.69 Å. The PgC_4 molecule of the asymmetric unit is donating three hydrogen bonds to three symmetry related $[HSO_4]^-$ ions with O···O distances of 2.71, 2.73, and 2.79 Å. The PgC_4 molecule is also donating three hydrogen bonds to three symmetry related water molecules which have O···O distances of 2.73, 2.86, and 2.86 Å. Two of the remaining six hydroxyl groups of the PgC_4 are donating hydrogen bonds to hydroxyl groups of neighbouring macrocycles with O···O distances of 2.88 and 2.97 Å. The four remaining hydroxyl groups are participating in intramolecular hydrogen bonds around the upper-rim of the macrocycle with O···O distances in the range of 2.63-2.87 Å.

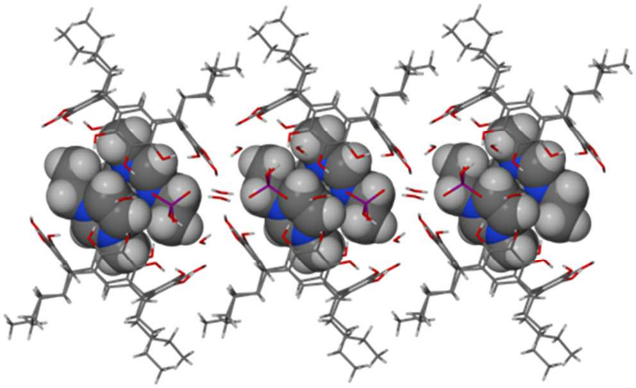

Fig. 12 Packing of cocrystal **6**, PgC_4·$[emim]^+$·$[HSO_4]^-$·$2H_2O$, viewed along the *a* axis. The guests are displayed in space-filling representation.

The host–guest complexes have stacked into bilayers as slightly offset dimers (see **Fig. 12**). Two of the hydrogen bonds being donated to $[HSO_4]^-$ ions are related to the opposing macrocycle in each dimer through the inversion centre, yielding four hydrogen bonds holding the dimers together (see **Fig. 13a**). The guest $[emim]^+$ ions in each dimer are close enough, 3.93 Å, to be interacting through π···π stacking (see **Fig. 13a**). There are four non-covalent host–guest interactions between the PgC_4 host and the $[emim]^+$ guest. These consist of two C–H···O and two C–H···π interactions (see **Fig. 13b**). Both C–H···π interactions occur through the donation of methyl hydrogen atoms of the guest to opposing pyrogallol moieties. The C–H···π aromatic centroid distances are 2.70 and 2.88 Å. The two C–H···O hydrogen bonds occur through the donation of an aromatic hydrogen atom of the guest and a hydrogen atom of the ethyl group of the guest to the host. The C–H···O distances of these interactions are 2.47 and 2.75 Å, respectively.

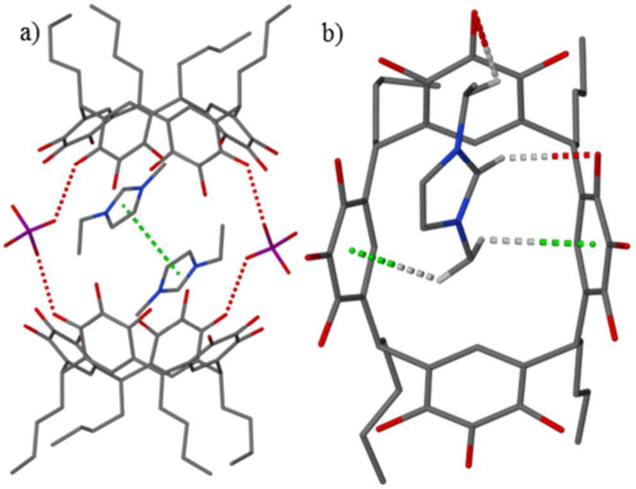

Fig. 13 a) Stick representation of the dimeric host-guest complex found in cocrystal **6**, PgC_4·$[emim]^+$·$[HSO_4]^-$·$2H_2O$, with the hydrogen bonds to the sulphate counter-ions shown as dashed red bonds and guest π···π interactions shown as dashed green bonds. b) The host-guest complex found in cocrystal **6** displayed in stick representation illustrating the host-guest interaction as dashed bonds. Hydrogen atoms not involved in interactions are hidden for clarity.

Cocrystal 7

Cocrystal **7** forms by crystallisation of a mixture of [emim][$EtSO_4$] and PgC_4OH in a solution of acetonitrile which results in a 2:1 host–guest complex packing into a bilayer structure in the space group P-1 (see **Fig. 14**). The asymmetric unit contains a PgC_4OH, a half occupancy $[emim]^+$ ion, a half occupancy $[EtSO_4]^-$ ion, one and a half of an acetonitrile molecule, and one water molecule. This and cocrystal **4** are the only two host–guest cocrystals presented here that form 2:1 complexes. In **4** the ratio of host:$[emim]^+$ remained at 1:1 due to the need for an extra exterior cation to balance the formation of sulphate ion. Similar to the host–guest complex in **4** the guest suffers from whole body disorder in the cavity formed by the two macrocycles. Here the disorder occurs over an inversion centre resulting in the two positions being present in equal amounts and due to the macrocycles being symmetry related, the interactions of both positions are equivalent. The $[EtSO_4]^-$ counter ion also exhibits disorder over the inversion centre and shares the two positions with a disordered acetonitrile molecule. This is the only cocrystal described here where the ILs anion is not hydrogen bonded to the upper-rim of the macrocycles. Instead, the $[EtSO_4]^-$ ion resides between the tails of two macrocycles accepting hydrogen bonds from the hydroxyl-footed tails and a water molecule. The three hydrogen bonds from the PgC_4OH tails have O···O distances of 2.58, 2.75, and 2.80 Å. The hydrogen bond donated by the water molecule has a O···O distance of 2.55 Å. The two macrocycles that comprise each dimer are not participating in hydrogen bonding directly to one another but rather hydrogen bond to neighbouring macrocycles, two water molecules, and a solvent acetonitrile. The two hydrogen bonds to water molecules have O···O distances of 2.68 and 2.72 Å. There is also a single hydrogen bond to an O···N distance of 2.89 Å. There are two hydrogen bonds being donated to the both the upper-rim and tail hydroxyls of neighbouring PgC_4OH macrocycles. The O···O distances of these interactions are 2.78, 2.80, 2.68, and 2.78 Å, respectively. The remaining five upper-rim hydroxyls of the asymmetric PgC_4OH molecule are intramolecular hydrogen bonds around the upper-rim and have O···O distances in the range of 2.70-2.81 Å.

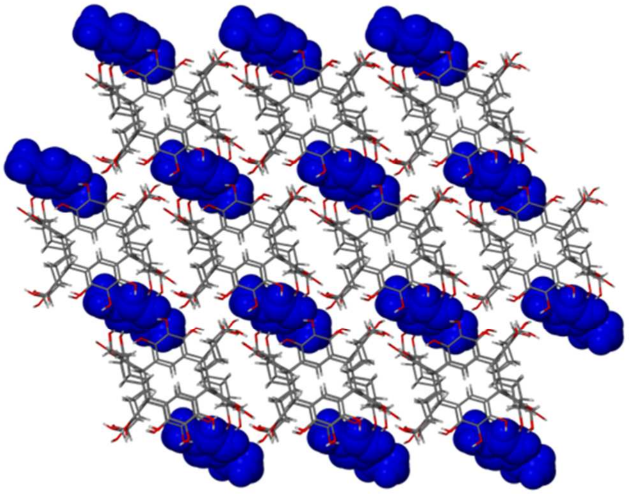

Fig. 14 Symmetry-generated packing of cocrystal **7**, $PgC_4OH{\cdot}0.5[emim]^+{\cdot}0.5[EtSO_4]^-{\cdot}H_2O{\cdot}1.5C_2H_3N$, as viewed along the [1 1 1] direction. Guest $[emim]^+$ ions are displayed as blue atoms in space-filling representation.

As mentioned in the previous paragraph, cocrystal **7** contains a dimeric host–guest complex where two PgC_4OH macrocycles complex a single $[emim]^+$ ion. There are seven noncovalent interactions; two C–H···π and five C–H···O interactions (see **Fig. 15**). The two C–H···π and two of the C–H···O hydrogen bonds occur between the ethyl chain of $[emim]^+$ ion and one of the macrocycles. The C–H···π distances here are 2.66 and 2.81 Å. The two C–H···O distances are 2.69 and 2.87 Å. One of the remaining C–H···O hydrogen bonds is being donated to this same macrocycle from one of the imidazolium hydrogen atoms with a H···O distances of 2.50 Å. Both of the remaining C–H···O hydrogen bonds are donated from the remaining two imidazolium hydrogen atoms to the second macrocycle and have C–H···O distances of 2.45 and 2.59 Å.

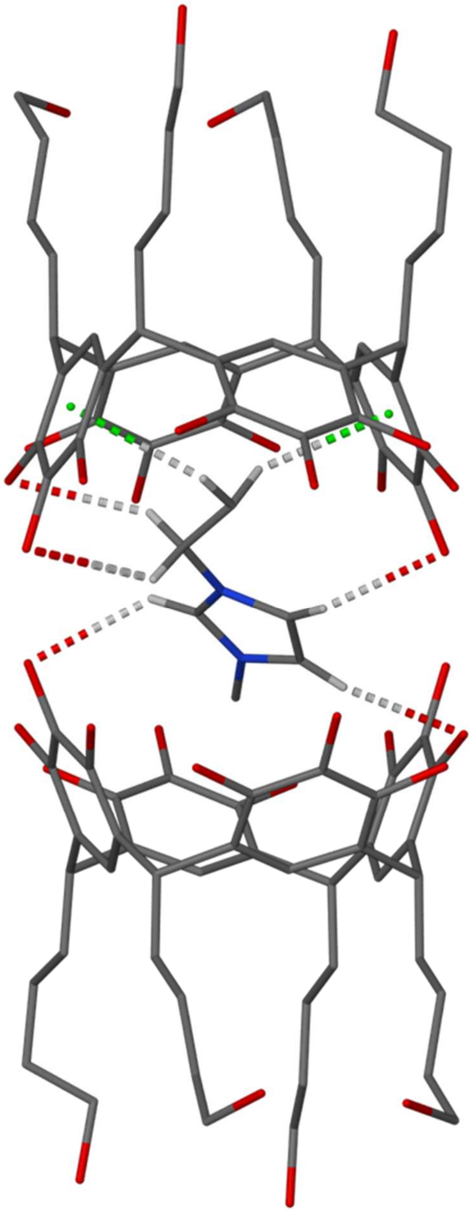

Fig. 15 Stick representation of a dimeric host-guest complex found in cocrystal **7**, $PgC_4OH{\cdot}0.5[emim]^+{\cdot}0.5[EtSO_4]^-{\cdot}H_2O{\cdot}1.5C_2H_3N$, with the observed non-covalent interactions shown as dashed bonds. Hydrogen atoms not involved in interactions have been hidden for clarity.

Discussion

As mentioned in the introduction, the initial efforts to synthesise PgC_xs/[emim][$EtSO_4$] host–guest cocrystals were carried out using the IL as the solvent. The inspiration for attempting such experiments originates from the report of the recyrstallisation of p-*tert*-butylcalix[4]arene in a solvent that is excluded from the crystal.[17] The resulting high density polymorph was found to be susceptible to single crystal phase transformations when subjected to high pressures of certain gases.[18] Recrystallisation of PgC_xs without solvent could potentially provide polymorphs with interesting structures, i.e. guest free capsules. However, the growth of crystals in an IL is complicated by the negligible vapour pressure and thus requires saturation of the macrocycle at elevated temperatures. Many attempts yielded poor quality crystals, often times very weakly diffracting due to highly disordered structures. In an attempt to resolve this, a PgC_x with an aromatic tail group, PgC_2Ph, was employed in hope that it would provide more sites for interactions with the lower-rim, i.e. $\pi \cdots \pi$ stacking and would aid in providing more ordered structures.

The results presented here, do offer useful observations about the host–guest systems of pyrogallol[4]arenes and [emim][$EtSO_4$]. While cocrystal **1** obviously stands alone in the synthetic method employed when compared to the other cocrystals reported, similarities can be seen in the host–guest complex itself such as the positioning of the guest $[emim]^+$ ions within the cavity of the PgC_xs. In cocrystal **1** the ethyl and methyl appendages are the portion of the guest that sits lowest in the bowl. This is also the case with cocrystals **4**, **6**, and **7**. All have different tail lengths and vary by solvent employed. In the remaining three cocrystals, the C_4–C_5 bond of the imidazolium ring is the portion of the guest that is positioned at the base of the macrocycle's bowl-shaped cavity. Our previous work revealed that multiple guest positions within the same cocrystal was possible and would even influence crystal packing.[15,16] Due to the fact that both positions are observed in cocrystals synthesised in acetone and acetonitrile there is no direct correlation as to whether it is influenced by the solvent employed. It should be noted that for both PgC_1 cocrystals the guest is positioned with the C_4–C_5 bond at the base of the bowl, the two PgC_2 cocrystals are split between this and the appendages at the base, and the longer chains have the appendages at the base. Our previous results showed that if the two positions are close enough in energy to both exist in the same crystal structure, then the packing is likely to have a strong influence in how the host–guest complex crystallizes. Thus chain length could have an indirect influence on the guest's position.

Another immediately noticeable difference between the cocrystals is the host:guest ratio. Due to the hydrolysis of the $[EtSO_4]^-$ ions in both **2** and **4** there are two counter ions and in both structures one is a guest while the second resides in the space between the bilayers. In **2** the guest is included within a single macrocycle. However, in **4** the guest ion is included within a pair of PgC_2 macrocycles forming an offset dimeric host–guest complex, packing into a bilayer-type structure.

There are also minor differences in the disorder in the structures of cocrystal **3** and **5**. In **5** the ethyl group of the $[EtSO_4]^-$ and the carbon atoms of the acetonitrile molecule are disordered over two positions. However this is trivial and could possibly due to the need to fill the small amount of extra void space from the expanded unit cell. In **3** the ethyl and methyl groups of the guest $[emim]^+$ ion are disordered over two positions with the major contribution at 80% occupancy. This is notable due to this position being quite similar to the sole guest position in **5**. This similarity is particularly noticeable when comparing the non-covalent interactions between the host and guest. Of which there are six in both structures and with the exception of one, occur at the same relative positions (see **Fig. 7** and **10**).

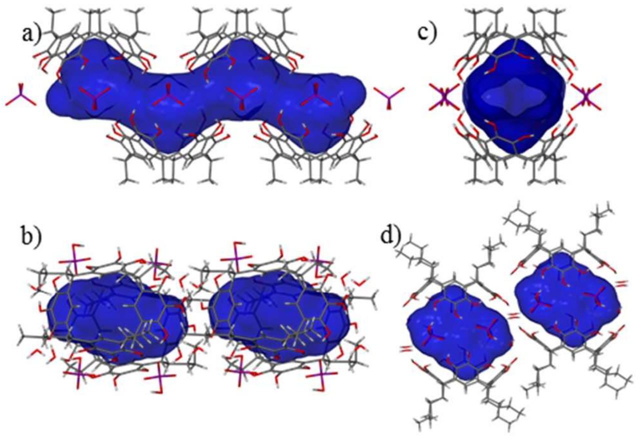

Fig. 16 a) and b) Alternate views of the packing pattern of cocrystal **2**, $0.5PgC_1{\cdot}1.5[emim]^+{\cdot}0.5[SO_4]^{2-}{\cdot}H_2O{\cdot}1.5C_3H_6O$, with the voids of the guest cavities displayed in blue. c) and d) Alternate views of the packing pattern of cocrystal **7**, $PgC_4OH{\cdot}0.5[emim]^+{\cdot}0.5[EtSO_4]^-{\cdot}H_2O{\cdot}1.5C_2H_3N$, with the voids of the guest cavities displayed in blue.

In all three reported cocrystals where acetone was used as the solvent the $[EtSO_4]^-$ ion undergoes hydrolysis forming a sulphate ion. Despite this, each of these structures is quite different when considering guest position and the type or ratio of the host–guest complexes. This is quite dissimilar from the cocrystals where acetonitrile was used. In the case of the **3** and **5** the two cocrystals are essentially isostructural. It is not surprising that the last cocrystal where acetonitrile was used, **7**, is quite different in structure from the other two. This is easily accounted for by the hydroxyl-footed tail of the PgC_4OH tails having a significant effect on the hydrogen bonding and packing of the crystal structure.

Another observation that immediately stands out relates to the cavities where the guest $[emim]^+$ ions reside in the various crystal systems. Throughout this report several of the cocrystals have been referred to as having packed such that the host–guest complexes form offset dimers. This is observed in all but one cocrystal reported here. To determine this, the program X-Seed[19] was used to generate packing pattern of each cocrystal structure. Guest molecules were subsequently removed from two adjacent dimers or in the case of cocrystal **2** four adjacent host–guest complexes. The program MSroll[20] was the used to calculate the void volume which the guests reside in, using a sphere with a radius of 1.5 Å. This was completed to determine if these voids were present as distinct voids separated by other constituents of the cocrystals, i.e. solvent or macrocycles. Cocrystal **2** stands out due to it having the distinction of being the only structure where the guests reside in 1-D channels (see **Fig. 16**). In all other cocrystals the offset dimers generate distinct voids (see **Fig. 16**). Also of note, is that the voids created by the host–guest complexes in **4** and **7** are significantly less than those in the other cocrystals. This is expected since there are the two cocrystals that form 2:1 host:guest ratio complexes. These would require less space than the 1:1 ratio complexes.

In order to establish whether the guests were affecting the geometry of the macrocycles, the cross-sectional distances were

Table 1 Cross-sectional distances of PgC_xs in various cocrystals related to guest positions.

	L × W (Å)	Guest Position
Previously Reported		
1a[15]	6.32 × 7.38	Ethyl/Methyl
1b[15]	6.26 × 7.35	C_4–C_5 Bond
2[16]	5.93 × 7.53	C_4–C_5 Bond
Cocrystal		
1	6.58 × 7.17	Ethyl/Methyl
2	6.64 × 7.02	C_4–C_5 Bond
3	5.98 × 7.43	C_4–C_5 Bond
4a	6.88 × 7.00	Ethyl/Methyl
4b	6.49 × 7.08	Ethyl/Methyl
5	6.00 × 7.47	C_4–C_5 Bond
6	6.17 × 7.33	Ethyl/Methyl
7	6.19 × 7.34	Ethyl/Methyl

measured. This was done by calculating the macrocycles' π-centroids for the benzene rings and measuring the distance between opposing ones. Table 1 offers a comparison of these distances and includes distances from our previously reported cocrystals as well as the relative guest positions within the bowl-shaped cavity of the pyrogallol[4]arene hosts. There are two positions of the guest molecules seen in these cocrystals. The first is with the ethyl or methyl appendages positioned deepest within the cavity of the macrocyclic host. The second is where the C_4–C_5 bond of the imidazolium ring is positioned deepest within the cavity. The shape of the macrocycle resides between the C_2-symmetrical "pinched-cone" and the C_4-symmetrical "cone" conformations. The variables that could have an effect on the shape of the macrocycles could include not only guest position but also tail length and crystallisation solvent as well as others. The position of the guest is of particular interest in these host–guest complexes. However, no definite pattern has emerged. The most "pinched" conformation observed to date was observed in the previously reported structure where a di-cation was complexed as the guest. This shape was very similar to the shape of the PgC_1 observed in cocrystal **3**. In both of these structures the guest position is with the C_4–C_5 bond deepest within the cavity of the host. The most symmetrical "cone conformation observed is seen in cocrystal **4** where the guest is positioned with the ethyl/methyl groups deepest within the cavity. The conformations of the pyrogallol[4]arenes seemingly trend in this way towards "pinched cone" for the C_4–C_5 bond and "cone" for alkyl appendages. There is overlap in the conformations when related to both of these guest positions. Our previous report wherein the host–guest complexes separated into distinct bilayers based on guest position could have foreshadowed this result. In that structure the shapes of the macrocycles were nearly identical and yet the host–guest complexes were able to self-assemble in to bilayers consisting of other complexes with the same guest position.[15] Cocrystals **3** and **5** have very similar shapes. This would be expected due to the two cocrystals being isostructural. Interestingly, in cocrystal **4** where there are two PgC_2 molecules in the asymmetrical unit, one of the macrocycles has a much less pinched conformation than the other. It would appear that multiple conditions are effecting the shape in each cocrystal and as of yet there is not a specific trend emerging.

Conclusions

The seven novel cocrystals formed by host–guest interactions between pyrogallol[4]arenes and a single ionic liquid component (1-ethyl-3-methylimidazolium ethylsulfate) presented herein highlight how small changes in cocrystal conditions can exert a surprising influence over the final supramolecular architecture. Continued investigations into solvent conditions, macrocycle functionality, and the chemistry of the ionic liquid component itself are expected to provide even more interesting opportunities for supramolecular assembly.

Experimental

Synthesis of pyrogallol[4]arene

All pyrogallol[4]arenes were synthesised according to literature procedures. PgC_1, PgC_2, PgC_2Ph, and PgC_4 were synthesised using the method reported by Gerkensmeier *et al.*[1] modified by selection of relevant aldehydes. PgC_4OH was synthesized using a modified procedure reported by Gibb *et al.*[21]

Synthesis of [emim][$EtSO_4$]

[emim][$EtSO_4$] was prepared according to a slightly modified literature procedure.[22] Briefly, 92.47 g (0.60 mol) of cold diethylsulfate was added dropwise over ~50 min to 48.75 g (0.59 mol) of 1-methylimidazole in toluene (175 mL) that had been pre-chilled to –15 °C in a conventional freezer. The reaction flask was immersed in an ice bath under argon in order to maintain a temperature below 25 °C during reaction (*Caveat:* the reaction is highly exothermic). After addition of diethylsulfate was complete, the ice was allowed to melt and the reaction mixture was stirred at room temperature for 3–4 h. Reaction monitoring by thin-layer chromatography confirmed completion of the reaction. The upper organic phase of the mixture was decanted and the lower phase was collected and washed several times with ethyl acetate (5 × 50 mL). After the last washing, the remaining ethyl acetate was removed by rotary evaporation. The as-prepared material was wetted with 100 mL of deionized water and stirred overnight with 9.87 g of Darco® G-60 activated carbon, followed by vacuum filtration to remove the carbon. The so-obtained IL was dried initially by heating to 40 °C overnight with stirring under high vacuum followed by an additional drying period of 70 °C for 24 h (still under vacuum) to yield a visually colorless fluid with a water content significantly less than 100 ppm by the Karl-Fischer method.

Synthesis of cocrystals

Single crystal X-ray diffraction quality crystals of cocrystal **1** were obtained by saturating 1.6 g of PgC_2Ph in 5 g of [emim][EtSO4] at 100 °C. The solution was then allowed to stir at 100 °C for 30 min to remove any residual solvent from the synthesis and crystallisation of the pyrogallol[4]arene.

Single crystal X-ray diffraction quality crystals of cocrystal **2** were obtained by sonication of a 1:1 mole ratio solution of PgC_1

and [emim][$EtSO_4$] in MeOH for 30 min. The resulting solution was then allowed to evaporate under ambient conditions.

Single crystal X-ray diffraction quality crystals of cocrystal **3** were obtained by sonication of a 1:1 mole ratio solution of PgC_1 and [emim][$EtSO_4$] in acetonitrile followed by addition of 1 mL of water to aid in dissolution. The resulting solution was then allowed to evaporate under ambient conditions.

Single crystal X-ray diffraction quality crystals of cocrystal **4** were obtained by sonication of a 1:1 mole ratio solution of PgC_2 and [emim][$EtSO_4$] in acetone. The resulting solution was then allowed to evaporate under ambient conditions.

Single crystal X-ray diffraction quality crystals of cocrystal **5** were obtained by sonication of a 1:1 mole ratio solution of PgC_2 and [emim][$EtSO_4$] in acetonitrile followed by addition of 1 mL of water to aid in dissolution. The resulting solution was then allowed to evaporate under ambient conditions.

Single crystal X-ray diffraction quality crystals of cocrystal **6** were obtained by sonication of a 1:1 mole ratio solution of PgC_4 and [emim][$EtSO_4$] in acetone. The resulting solution was then allowed to evaporate under ambient conditions.

Single crystal X-ray diffraction quality crystals of cocrystal **7** were obtained by sonication of a 1:1 mole ratio solution of PgC_4OH and [emim][$EtSO_4$] in acetonitrile followed by addition of 1 mL of water to aid in dissolution. The resulting solution was then allowed to evaporate under ambient conditions.

Crystallography

The single crystal X-ray diffraction data for cocrystals **1**, **2**, and **5-7** were collected with a Bruker Apex II CCD diffractometer using Mo Kα radiation. Data for cocrystals **3** and **4** were collected with a Bruker Apex II CCD diffractometer using synchrotron radiation, $\lambda = 0.77490$ Å. See Table 2 for further crystallographic information.

Table 2 Crystallographic Information

Cocrystal	**1**	**2**	**3**	**4**	**5**	**6**[a]	**7**
Empirical formula	$C_{84}H_{110}N_6O_{27}S_3$	$C_{50}H_{70}N_4O_{20}S$	$C_{42}H_{53}N_3O_{17}S$	$C_{87}H_{122}N_4O_{36}S$	$C_{46}H_{61}N_3O_{17}S$	$C_{50}H_{72}N_2O_{18}S$	$C_{102}H_{141}N_5O_{37}S$
Formula weight	1731.96	1079.16	903.93	1831.95	960.04	1021.16	2061.26
Temperature (K)	173(2)	173(2)	100(2)	100(2)	173(2)	173(2)	173(2)
Crystal system	monoclinic	monoclinic	triclinic	monoclinic	triclinic	monoclinic	triclinic
Space group	$P2_1/n$	$P2/c$	P-1	Cc	P-1	$P2_1/c$	P-1
Unit cell dimensions (Å, °)							
a =	12.720(3)	12.328(5)	9.9102(15)	19.3218(16)	10.0590(19)	21.075(9)	12.821(4)
b =	39.701(10)	16.545(7)	14.121(2)	14.7252(12)	14.556(3)	12.796(6)	13.060(4)
c =	16.861(4)	12.821(5)	14.877(2)	32.896(3)	15.558(3)	18.229(8)	17.065(9)
α =	90.00	90.00	91.328(2)	90.00	92.816(2)	90.00	103.536(6)
β =	95.212(4)	109.190(5)	96.132(2)	104.855(2)	93.863(2)	96.533(6)	100.638(6)
γ =	90.00	90.00	96.436(2)	90.00	96.287(2)	90.00	109.687(4)
Volume (Å^3)	8480(4)	2469.7(17)	2055.7(5)	9046.6(14)	2255.5(7)	4884(4)	2505.0(17)
Z	4	2	2	4	2	4	1
Calculated density (g cm^{-3})	1.357	1.451	1.460	1.345	1.414	1.389	1.366
F_{000}	3680	1148	956	3904	1020	2184	1100
θ range for data collection (°)	1.59 to 26.51	1.75 to 27.59	2.91 to 29.81	2.84 to 31.51	1.87 to 27.54	1.87 to 25.01	1.75 to 26.40
Reflections collected	93067	28634	24409	52016	26045	40401	27643
Independent reflections	17540	5696	9039	26670	10156	8413	10214
R_{int}	0.0620	0.0507	0.0806	0.0683	0.0283	0.1380	0.0592
Goodness-of-fit on F^2	1.043	1.068	1.008	1.022	1.013	1.024	1.056
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0728$, $wR2 = 0.1867$	$R1 = 0.0668$, $wR2 = 0.2000$	$R1 = 0.0575$ $wR2 = 0.1400$	$R1 = 0.0766$ $wR2 = 0.2043$	$R1 = 0.0499$ $wR2 = 0.1268$	$R1 = 0.0934$ $wR2 = 0.2099$	$R1 = 0.0786$ $wR2 = 0.2169$
R indices (all data)	$R1 = 0.1209$, $wR2 = 0.2195$	$R1 = 0.0850$, $wR2 = 0.2194$	$R1 = 0.0936$ $wR2 = 0.1598$	$R1 = 0.0962$ $wR2 = 0.2276$	$R1 = 0.0840$ $wR2 = 0.1502$	$R1 = 0.2169$ $wR2 = 0.2636$	$R1 = 0.1496$ $wR2 = 0.2643$

[a] Cocrystal **6** was a multiple component crystal and the data was reduced using two domains. The HKLF4 and merging R-factor were generated using twinabs.

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Notes and references

[a] *University of Missouri, 601 South College Avenue, Columbia, Missouri, USA. Fax: 573 882 2754; Tel: 573 882 8374; E-mail: bakergar@missouri.edu; AtwoodJ@misssouri.edu*
[b] *Advanced Light Source, 1 Cyclotron Road, MS6R2100, Berkeley, California, USA. Fax: 510 486 4773; Tel: 510 486 7745; E-mail: sjteat@lbl.gov*

1 T. Gerkensmeier,W. Iwanek, C. Agena, R. Fröhlich, S. Kotila, C. Näther and J.Mattay, *Eur. J. Org. Chem.*, 1999, 2257.

2 S. J. Dalgarno, N. P. Power, J. E. Warren and J. L. Atwood, *Chem. Commun.*, 2008, 1539; J. L. Atwood, L. J. Barbour and A. Jerga, *Chem. Commun.*, 2001, 2376; N. P. Power, S. J. Dalgarno and J. L. Atwood, *New J. Chem.*, 2007, **31**, 17; S. J. Dalgarno, G. W. V. Cave and J. L. Atwood, *Angew. Chem., Int. Ed.*, 2006, **45**, 570; O. V. Kulikov, M.M. Daschbach, C. R. Yamnitz, N. Rath and G. W. Gokel, *Chem. Commun.*, 2009, 7497.

3 H. Kumari, A. V. Mossine, S. R. Kline, C. L. Dennis, D. A. Fowler, S. J. Teat, C. L. Barnes, C. A. Deakyne and J. L. Atwood, *Angew. Chem., Int. Ed.*, 2012, **51**, 1452.

4 P. Jin, S. J. Dalgarno, C. Barnes, S. Teat and J. L. Atwood, *J. Am. Chem. Soc.*, 2008, **130**, 17262.

5 J. L. Atwood, L. J. Barbour, M. W. Heaven and C. L. Raston, *Chem. Commun.*, 2003, 2270-2271; J. L. Atwood, L. J. Barbour and C. L. Raston, *Cryst. Growth Des.*, 2002, **2**, 3; H. Mansikkamäki, M. Nissinen and K. Rissanen, *CrystEngComm*, 2005, **7**, 519.

6 I. Ling, Y. Alias, A. N. Sobolev, L. T. Byrne and C. L. Raston, *CrystEngComm*, 2011, **13**, 787; I. Ling, Y. Alias, A. N. Sobolev and C. L. Raston, *CrystEngComm*, 2010, **12**, 1869; I. Ling, A. N. Sobolev, Y. Alias and C. L. Raston, *CrystEngComm*, 2013, **15**, 2888.

7 S. J. Dalgarno, S. A. Tucker, D. B. Bassil and J. L. Atwood, *Science*, 2005, **309**, 2037; D. A. Fowler, J. Tian, C. Barnes, S. J. Teat and J. L. Atwood, *CrystEngComm*, 2011, **13**, 1446; K. K. Kline, D. A. Fowler, S. A. Tucker and J. L. Atwood, *Chem.–Eur. J.*, 2011, **17**, 10848; A. V. Mossine, H. Kumari, D. A. Fowler, A. K. Maerz, S. R. Kline, C. L. Barnes and J. L. Atwood, *Isr. J. Chem.*, 2011, **51**, 840; A. Åhman, M. Luostarinen, K. Rissanen and M. Nissinen, *New J. Chem.*, 2007, **31**, 169.

8 E. Ahmed, J. Breternitz, M. F. Groh and M. Ruck, *CrystEngComm*, 2012, **14**, 4874; M. Kowacz, P. Groves, J. M. S. S. Esperancua and L. P. N. Rebelo, *Cryst. Growth Des.*, 2011, **11**, 684.

9 R. E. Del Sesto, T. M. McCleskey, A. K. Burrell, G. A. Baker, J. D. Thompson, B. L. Scott, J. S. Wilkes and P. Williams, *Chem. Commun.*, 2008, 447.

10 W. M. Reichert, J. D. Holbrey, K. B. Vigour, T. D. Morgan, G. A. Broker and R. D. Rogers, *Chem. Commun.*, 2006, 4767.

11 S. Saha, S. Hayashi, A. Kobayashi and H. Hamaguchi, *Chem. Lett.*, 2003, **32**, 740; J. Dupont, *J. Brazil. Chem. Soc.*, 2004, **15**, 341.

12 F. C. Gozzo, L. S. Santos, R. Augusti, C. S. Consorti, J. Dupont and M. N. Eberlin, *Chem. Eur. J.*, 2004, **10**, 6187.

13 R. E. Morris, *Chem. Commun.*, 2009, 2990.

14 For a 10-article collection bringing together a series of papers showcasing recent advances in the use of ILs in crystal engineering, see: *CrystEngComm*, 2012, **14**, 4873.

15 D. A. Fowler, S. J. Teat, G. A. Baker and J. L. Atwood, *Chem. Commun.*, 2012, **48**, 5262.

16 D. A. Fowler, J. L. Atwood and G. A. Baker, *Chem. Commun.*, 2013, **49**, 1802.

17 E. B. Brouwer, K. A. Udachin, G. D. Enright, J. A. Ripmeester, K. J. Ooms and P. A. Halchuk*, Chem. Commun.*, 2001, 565.

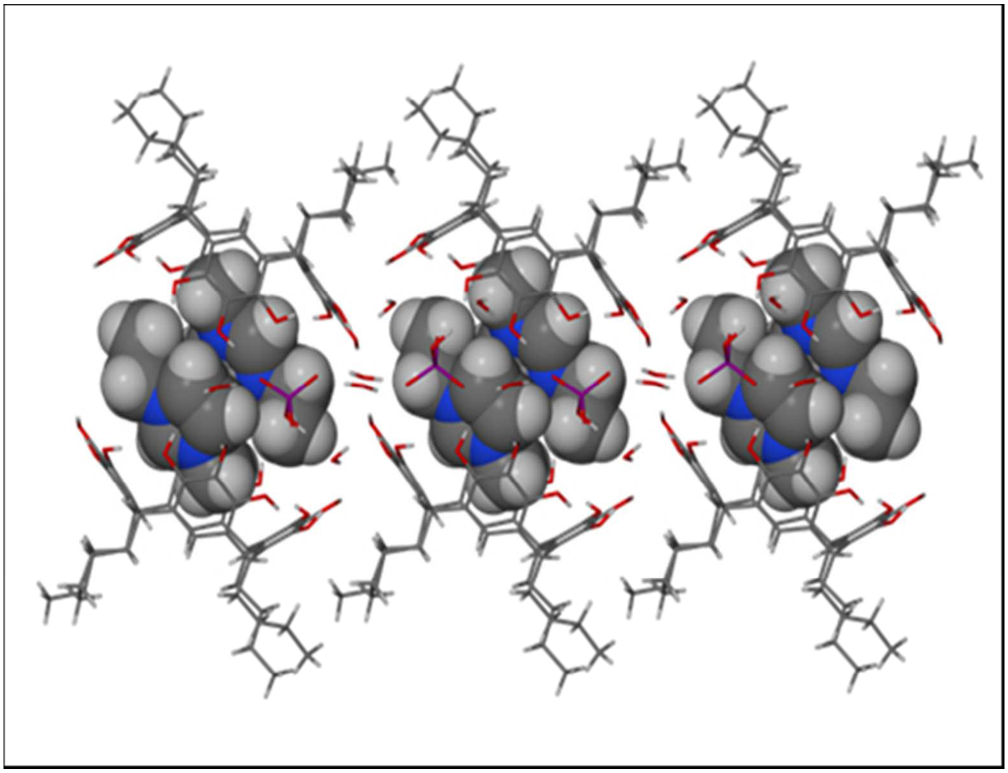
18 P. K. Thallapally, B. P. McGrail, S. J. Dalgarno, H. T. Schaef, J. Tian and J. L. Atwood, *Nat. Mater.*, 2008, **7**, 146.

19 L. J. Barbour, *J. Supramol. Chem*. 2001, **1**, 189.

20 M. L. Connolly, *J. Mol. Graph*. 1993, **11**, 139.

21 B. C. Gibb, R. G. Chapman and J. C. Sherman, *J. Org. Chem*., 1996, **61**, 1505.

22 J. D. Holbrey, W. M. Reichert, R. P. Swatloski, G. A. Broker, W. R. Pitner, K. R. Seddon and R. D. Rogers, *Green Chem.*, 2002, **4**, 407.



Symmetry-generated packing of a cocrystal composed of C-butyl-pyrogallol[4]arene and the ionic liquid, 1-ethyl-3-methylimidazolium ethylsulfate.
89x68mm (150 x 150 DPI)