Recent advances in self–assembled amidinium and guanidinium frameworks

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The amidinium and guanidinium groups are strong and potentially directional hydrogen bond donors that have proven useful in anion recognition and solution phase self–assembly, and more recently in the synthesis of supramolecular frameworks. This Frontier article gives a background to the use of these groups in framework synthesis, describes recent advances in the field, and looks to future directions in this area.

Introduction

Hydrogen bonds are individually relatively weak, but together may be used to give stable self–assembled systems.[1] While the use of hydrogen bonds to assemble network materials has not received the same level of attention as metal–templated framework assembly,[2-4] a wide range of well-ordered materials have been prepared. In pioneering work in the early 1990s Wuest demonstrated that carefully-designed tectons containing self-complementary hydrogen bonding motifs could give 3D materials containing large channels.[5-7] Since then, a range of hydrogen bonded frameworks (HOFs)[8,9] have been prepared, and some of these have been shown to be permanently porous and/or have remarkably high stabilities.[10-14]

Although the vast majority of these frameworks have been formed from the assembly of a single neutral molecule, an alternative approach is to use two (or more) charged components to assemble the network structure. This approach is similar to that used in coordination polymer/MOF chemistry where both a cationic and anionic component are used, and it offers a couple of key potential advantages over assembly from one neutral component. Firstly, charged hydrogen bonds may be significantly stronger than neutral ones due to the addition of electrostatic attractions, and secondly that the use of two components may allow modular synthesis of related frameworks (cf. isoreticular synthesis of MOFs).[3]

There have been a range of materials prepared from protonated amine/pyridine components with various anions,[15-20] but this article will focus on recent advances in systems prepared from amidinium and guanidinium cations (Fig. 1).[‡] These cations have relatively high pK_as so remain protonated under neutral conditions, and offer the prospect of predictable self–assembly due to their (potentially) well-defined hydrogen bonding geometries. In particular, they can form robust "paired" hydrogen bonds with carboxylate or sulfonate anions.

Over the last two decades, the Ward group has used unsubstituted guanidinium cations and sulfonate anions to prepare a range of elegant crystalline materials (Fig. 2a,b),[21-23] The cation can assemble into 2D layers with sulfonate anions, and judicious use of polysulfonate anions gives a range of

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pillared materials that showed interesting host–guest behaviour. Additionally, the guanidinium motif has been thoroughly investigated in the context of anion recognition.[24-27]

While it has been less studied than the guanidinium group, the interaction of amidiniums with carboxylates has been used to prepare a range of self–assembled structures including capsules, catenanes and helices (Fig. 2d).[28-34] Amidinium groups have also been used to prepare solid state architectures, with pioneering work by Wais Hosseini showing that cyclic bis(amidiniums) can be assembled into 1D and 2D structures with carboxylate anions (Fig. 2c).[35-37]

This Frontier article gives a brief introduction to the guanidinium and amidinium groups, highlights significant recent advances in self–assembled frameworks containing these motifs, then considers the future possibilities for this area of research.
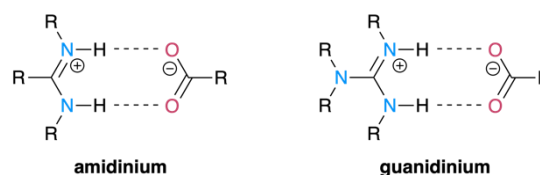

Fig. 1 Structures of guanidinium and amidinium cations used in self–assembly applications, and typical "paired" hydrogen bonding interactions with carboxylate anions.

Synthesis and fundamental properties

Guanidinium and amidinium compounds differ only in the nature of the substituent at the central carbon atom, with amidinium cations containing two nitrogen atoms bonded to this carbon, while guanidiniums have three (Fig. 1). For self–assembly applications such as those discussed in this article, the amidinium group has predominantly been used as the benzamidinium derivative, both for ease of synthesis and the directionality imparted by the lack of a flexible group.

Both guanidinium and benzamidinium moieties have pK_a values in an ideal range for charge-assisted hydrogen bonding: low enough that they are potent hydrogen bond donors, but high enough to minimize problems caused by deprotonation. The pK_a of benzamidinium is significantly lower than that of guanidinium (11.6 vs. 13.7), presumably caused by the aromatic substituent present in benzamidinium.[38] In fact, phenylguanidinium is even more acidic than benzamidinium (pK_a 10.9), although for synthetic reasons this cation has seen little use in supramolecular chemistry.
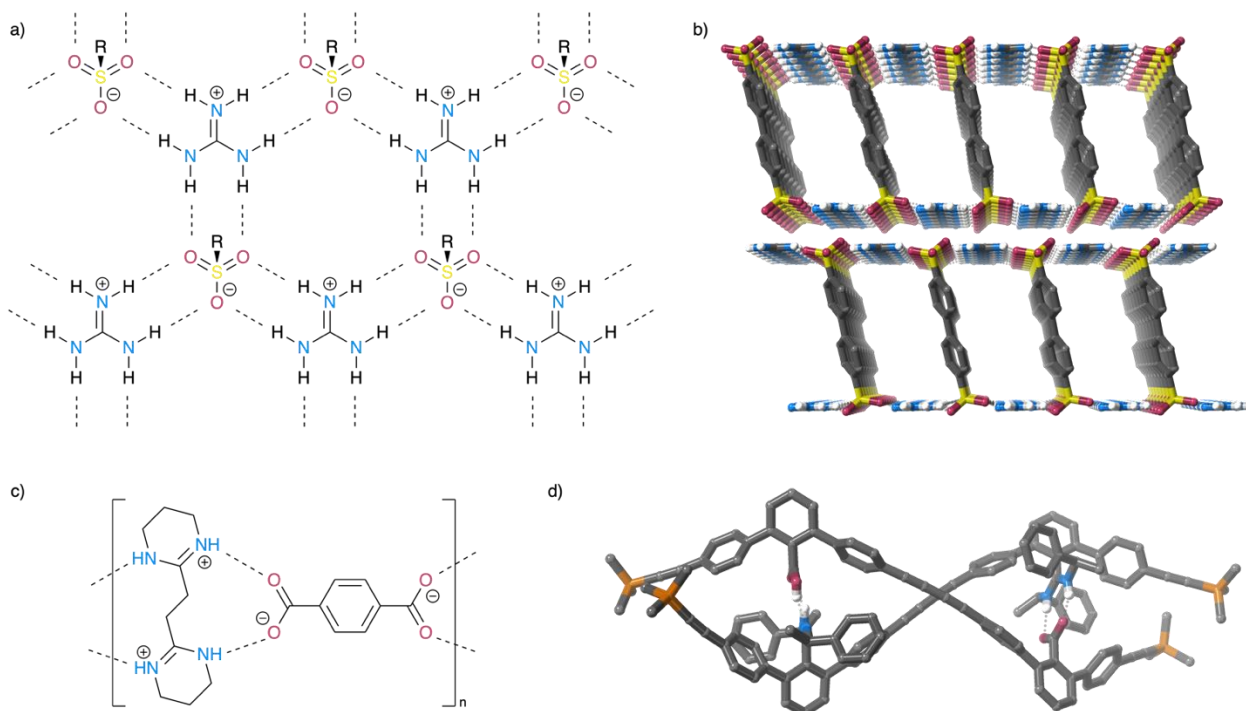
Fig. 2 Important early work using amidinium or guanidinium groups for self–assembly: a) general structure of Ward's GS frameworks; b) X-ray crystal structure of GS framework prepared from 4,4′-biphenyldisulfonate; c) example of a 1D polymeric system prepared by Wais Hosseini; d) X-ray crystal structure of double helix structure prepared by Yashima (most hydrogen atoms, guests and solvent molecules omitted from crystal structures).
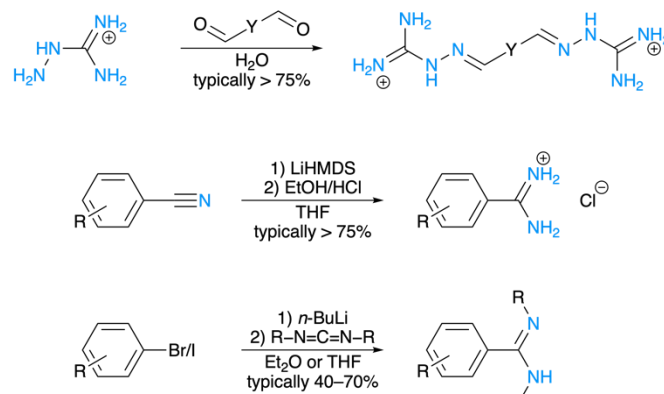
Synthesis

Most of the self–assembled guanidinium systems reported to date fall into two categories, they are either simple (*i.e.* unsubstituted) guanidinium cations that assemble with (poly)sulfonate anions, or iminoguanidinium systems, which are readily-prepared in high yields by the condensation of dialdehydes and commercially-available aminoguanidinium salts (Scheme 1).

The synthesis of amidine/amidinium groups is well-established and several different methodologies are known.[39] Of relevance to this article, my group has found that the reaction of benzonitriles with a commercially-available THF solution of LiHMDS and subsequent work-up with ethanolic HCl as described by Boykin[40] gives easy access to a wide range of (poly)amidiniums in high yields. Alternatively, Yashima has prepared a range of *N*-substituted benzamidiniums by lithium/halogen exchange of a halobenzene followed by reaction with carbodiimide moieties.[30]

Interactions in solution

The solution phase binding of guanidinium cations to anionic species has been thoroughly studied, as these groups have seen significant use in synthetic anion receptor systems.[27] Notably, poly(guanidinium) systems have been reported that can bind carboxylate anions with very high binding affinities in a range of solvents including aqueous buffer.[26,41] Unsubstituted guanidinium cation binds anions strongly in DMSO,[42] although shows only very weak association with carboxylates in water (K_a < 1).[43]

Scheme 1 Representative syntheses of bis(guanidinium), amidinium, and *N*-alkyl amidine compounds used in the preparation of self–assembled hydrogen bonded structures.

In contrast, the solution phase binding of (benz)amidinium groups to anions has been far less-studied. Strong binding between amidinium cations and carboxylate anions has been reported in DMSO,[44-46] while binding constants > 10^7 M^{-1} have been reported for an amidinium/carboxylate complex in acetonitrile/toluene mixtures.[47] We recently reported that simple *tert*-butylbenzamidinium displayed strong benzoate binding in 95:5 CH$_3$CN:H$_2$O (K_a = 2900 M^{-1})[48] although in pure water interactions between bis(amidinium) cations and dicarboxylate anions are negligible.[34,49] Molecular dynamics simulations of bis(amidinium) systems and carboxylates suggested that a range of hydrogen bonding geometries occur frequently in solution,[49] as has been previously observed in solid

state crystal structures of these compounds[50,51] (*i.e.* not just the idealised "paired" H-bonding geometry, Fig. 1).

Structural properties

To gain insight into the structural properties of hydrogen bonded complexes of amidinium and guanidinium cations in the solid state, a search of the Cambridge Structural Database[52] (CSD) was undertaken. The CSD was searched for structures containing either amidinium or guanidinium groups with hydrogen bonds to carboxylate and carbonate anions, or to sulfonate anions (see ESI for details of these searches and a more detailed analysis). The median H···O length in structures containing amidinium cations and carboxylate/carbonate anions is 1.93 Å, while that for structures containing guanidinium cations and carboxylate/carbonate anions is 2.03 Å. The H···O median distance for guanidinium···sulfonate hydrogen bonds is even longer, at 2.08 Å (there are only six structures containing amidinium···sulfonate hydrogen bonds in the database, so no analysis was made).

Most of these guanidinium structures contain either unsubstituted or alkyl-substituted cations, while a majority of the amidinium structures contain benzamidinium groups, so clearly a direct comparison cannot be made. Nonetheless, the significant difference in H-bond lengths may be a factor to consider when designing frameworks containing these groups.

Recent advances

Recent advances with guanidinium frameworks

In the last few years, there have been several important developments in the field of guanidinium sulfonate frameworks (Fig. 2a for general structure). In 2016, Ghosh reported two GS frameworks constructed from biphenyldisulfonate or naphthalenedisulfonate anions that were stable to evacuation and showed modest but selective CO_2 binding.[53] While the pores in the material are small (~15% of the cell volume), the demonstration of permanent porosity in such materials is a significant advance. Furthermore, the authors demonstrated that these frameworks showed very high proton conductivity.

Ward has previously shown that 3D frameworks can be assembled from hydrogen bonded cages prepared from guanidinium and sodium cations, and nitrate and hexa(4-sulfonatophenyl)benzene anions.[54§] These cages have the shape of truncated octahedra and have an interior volume of 2200 Å and can incorporate a wide range of guest species. In 2017, the same group expanded on this work and demonstrated that luminescent guests could also be incorporated in the framework.[55] Importantly, even when one luminophore was incorporated per cage (a solid state concentration equal to 0.175 mol L^{-1}), no aggregation-induced self-quenching was observed. This is a much higher concentration than that which leads to self-quenching in solution and may offer a route to efficient solid state organic lasers.

Continuing his pioneering work in this field, Ward studied a guest exchange process in a seemingly inaccessible GS framework: crystallisation of guanidinum cations and tris(4-sulfonatophenyl)benzene in the presence of isophorone gave the expected framework, which contained 3.7 isophorone guests per tris(sulfonate) anion.[56] Exposure of the crystals to hexafluorobenzene (HFB) resulted in partial exchange of the guests, although crystal structure analysis suggested that the starting framework was too densely-packed to allow conventional guest exchange. Detailed *in situ* optical microscopy and Raman spectroscopy studies revealed the high mobility of isophorone molecules close to the site of the incoming HFB molecules. The appearance of lamellae growing from the crystal perimeter was also observed during guest exchange and the authors concluded that these increased the speed of guest transfer.

Custelcean has prepared some very different guanidinium-containing frameworks: in 2015, he reported that sulfate and nitrate could be extracted from water by addition of aminoguanidinium and glyoxal, as the resulting ethyl-linked bis(guanidinium) compound formed an insoluble hydrogen-bonded network with these anions (as their hydrates).[57,58] In the last couple of years, this group has reported related systems that can complex CO_2 from the air as insoluble hydrogen-bonded networks containing carbonate anions.[59] Remarkably, when an aqueous solution of bis(guanidine) **1** was left open to air, large single crystals of the carbonate salt of the protonated bis(guanidinium) compound **1²ᴴ·CO₃·4H₂O** were formed (Fig. 3). The crystalline material forms an extended hydrogen-bonded framework with channels of hydrated carbonate anions surrounded by **1²ᴴ** molecules. Overall this gives approximately planar 2D sheets, which are linked together through water···carbonate hydrogen bonding. Despite the low concentration of atmospheric $CO_{2(g)}$ (~ 400 ppm), the very low solubility of the framework is sufficient to favour crystallization. Importantly, the CO_2 could be released and **1** recovered by mild heating of the crystals – an important improvement on many existing technologies, which require high temperatures to release the CO_2 (for subsequent storage) and recover the adsorbent.

Additionally, **1** could be used in conjunction with other CO_2 capture methodologies to increase their efficiency. Simple alkali metal carbonates in water can capture CO_2 by forming bicarbonate, with one molecule each of carbonate, CO_2 and H_2O combining to give two bicarbonate anions. Custelcean demonstrated that **1** can increase the efficiency of this capture technology by sequestering the carbonate from solution and precipitating it (again as **1²ᴴ·CO₃·4H₂O**), allowing for facile recovery of the trapped CO_2. In contrast, liberating CO_2 from alkali (bi)carbonates to regenerate the sorbent requires temperatures in excess of 800 °C. In a subsequent paper, it was demonstrated that **1** could be used in a similar process but using amino acids as the sorbent, and that this system combined with very simple equipment (an air humidifier and solar oven) could generate a functioning, cyclable CO_2 capture system.[60]
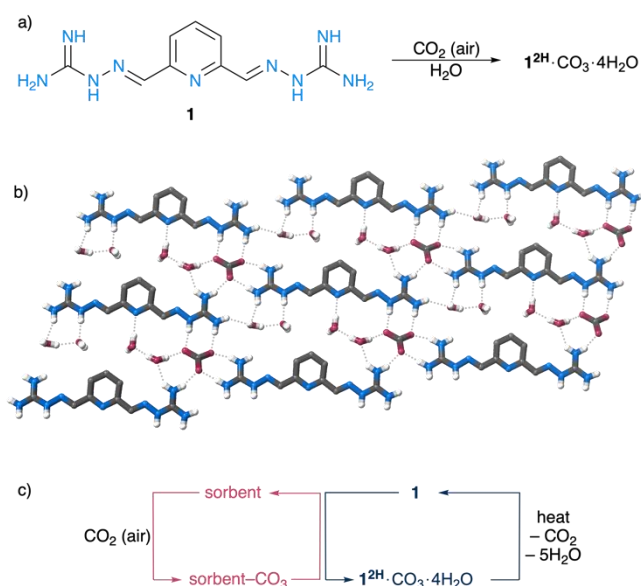
Fig. 3 Custelcean's CO_2 adsorbent: a) reaction scheme for CO_2 capture; b) X-ray crystal structure of CO_3-containing network (some hydrogen atoms omitted for clarity); c) schematic of cycle using **1** to improve the performance of traditional sorbent materials.

Recent advances with amidinium frameworks

My group has used the tetraamidinium tecton **2⁴⁺** and dicarboxylate anions to form three-dimensional diamondoid framework materials in water (Fig. 4).[48] Simple mixing of aqueous solutions of the two components led to rapid formation of crystals containing square channels, which are approximately 13 Å in diameter. A range of other anions (halides, nitrate, sulfate, isophthalate) did not lead to network formation suggesting considerable fidelity in the self–assembly process.

Further experiments revealed that this framework was actually a kinetically-trapped product, and that a denser thermodynamically-favoured framework could also be isolated. It was possible to switch between the two networks, and to disassemble and re-assemble the frameworks in response to various stimuli. Replacing terephthalate with smaller oxalate (**ox**²⁻) did not lead to the desired **2·ox₂** network, instead forming a mixed anion complex **2·ox·Cl₂**,[61] but using a square planar porphyrin tetracarboxylate tecton gave rise to a framework with the expected PtS topology (Fig. 4).[62] In this material, 75% of the unit cell volume is occupied by solvent, making it one of the most open hydrogen-bonded materials to date,[8] although it rapidly loses crystallinity on removal from solvent.

In 2018, Ben, Marchiò and Comotti showed that both guanidinium and amidinium cations could form network structures with polysulfonate anions in water and/or methanol.[63] Very recently, these authors combined the tetrasulfonate anion **3⁴⁻** with benzenebis(amidinium) **4²⁺** to give a 3D framework containing small (5 x 7 Å) helical channels (Fig. 4).[64] This material is highly stable and can be activated to give a porous material that absorbs CO_2 and displays a remarkable selectivity for CO_2 over N_2 (up to 690-fold). NMR experiments combined with DFT calculations showed very close contacts between the amidinium groups and CO_2, and revealed that the CO_2 molecules moved through the framework in a rapid screw-like motion.

Discussion

As these recent highlights show, there are clearly a range of different frameworks that can be accessed relatively easily from amidinium and guanidinium groups. It would appear that rigid benzamidinium groups are well-suited to the formation of designed framework materials particularly in conjunction with polycarboxylate anions, as both the cationic and anionic component can be varied, and there is a rigid directionality imposed along the benzamidinium···carboxylate axis. In theory this could lead to a wide range of materials with tuneable structure and topology, and first steps in this direction have allowed the predictable synthesis of diamondoid and PtS materials.

The guanidinium cation has been used to prepare a wide range of materials over the last two decades. In the case of the GS frameworks prepared by Ward, use of a range of elegantly-designed polysulfonate anions, and subtle tuning of guest molecules has given access to a wide range of framework topologies and structures despite the fact that the cationic component (unsubstituted guanidinium) remains constant.[23] Custelcean's systems contain very simple bis(guanidinium) cations and this simplicity allows them to be prepared cheaply and efficiently in one pot offering the possibility that they may useful for industrial CO_2 and/or anion capture processes.[57-60] It would be interesting to see whether incorporating further guanidinium cations around the central scaffold (and potentially moving into three dimensions) improves the extraction efficiency of these materials by further increasing the difference in solubility between the starting material and resultant framework.

As yet, most amidinium and guanidinium materials have not been permanently porous, *i.e.* they have collapsed upon solvent removal. Ghosh's GS frameworks and Ben, Sozzani and Commoti's amidinium–sulfonate framework are an exception to this, both showing permanent porosity and selective CO_2 binding.[53,64] Both these materials show relatively small solvent-accessible voids (~15% of the unit cell in both cases) and it may be that materials with relatively low porosity are the best immediate targets for future research in this area as the frameworks can withstand the loss of solvent more readily. Interestingly, **4·3₂** dissolves in DMSO, suggesting that the hydrogen bonds holding it together are not particularly strong;[64] in contrast our amidinium materials do not dissolve in boiling DMSO or water but collapse on drying.[48,62]

While to date very few amidinium/guanidinium framework materials have shown permanent porosity, it should be noted that highly porous hydrogen-bonded materials assembled from *neutral* components have been shown to be stable to evacuation.[12] Given that charge-assisted hydrogen bonds are stronger than regular hydrogen bonds, it would seem likely that highly porous materials stable to evacuation should be realisable. Most materials prepared to date from ionic components are crystallised from very polar solvents that are themselves capable of strong hydrogen bonding interactions, so careful activation protocols may be needed to give permanently porous materials.[65] Given the impressive CO_2 selectivity observed to date for amidinium and guanidinium frameworks,

preparing similar systems and investigating the scope and mechanism of gas binding would clearly be of interest.

Conclusions

The last few years have seen major advances in self–assembled frameworks prepared from amidinium and guanidinium groups, including in the fields of anion and CO_2 sequestration, proton conductivity and predictable framework design. While materials with high permanent porosities have not yet been obtained, many interesting uses for these frameworks have already been reported. Given the strong and predictable hydrogen bonding properties of the amidinium and guanidinium groups, there seems to be scope to design and prepare a broad range of functional supramolecular materials for a range of applications.

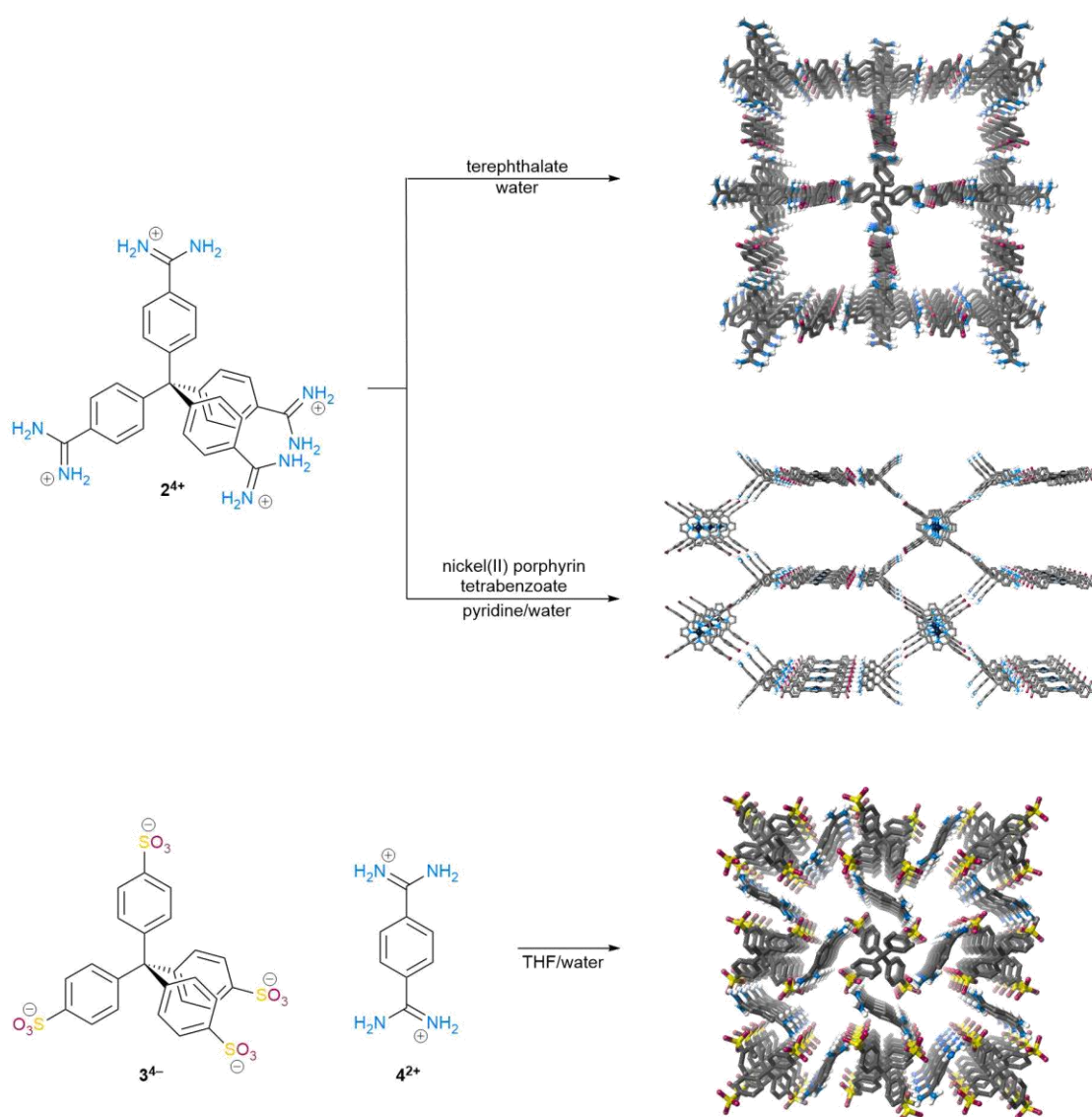## Conflicts of interest

There are no conflicts to declare.

Fig. 4 Structures of open 3D frameworks containing amidinium groups prepared by the groups of White, and Ben, Sozzani and Comotti.

Notes and references

‡ The materials described in this article exist in their protonated states (*i.e.* amidinium and guanidinium). In some cases, the materials are introduced as their neutral congeners (*i.e.* amidine

and guanidine) but undergo proton transfer to the cationic forms as part of framework formation.

§ These structures are slightly different to Ward's previous GS frameworks: three guanidinium cations form a 2+ tecton that incorporates a central nitrate anion. The cages prepared from this 2+ tecton and the 6− sulfonate anion are therefore negatively-charged overall, and are assembled into networks of cages by interactions between the sodium cations and sulfonate anions.

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