Open Frameworks Formed from Iodoalkyne–Halide Halogen Bonds

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Abstract: Despite the apparently attractive characteristics of halogen bonds for preparing open/porous framework structures, very few such materials containing substantial void space have been reported. Iodoalkynes are readily prepared halogen bond donors with rigid rod-like structures and form halogen bonded assemblies with halide anions, although these typically have densely-packed structures. Here we show that rigid tetratopic and hexatopic halogen bond donor molecules containing unactivated iodoalkyne groups give a family of highly open 2D and 3D structures, where up to 47% of the unit cell volume is made up of solvent-filled voids. Interestingly, several different framework topologies are observed, all with high void volumes, even when very similar starting materials are used. While in the current work, the frameworks lose crystallinity upon removal from solvent, we believe this is an important step towards highly porous halogen bonded materials.

Introduction

Inspired by the successes in the field of coordination polymers/metal organic frameworks (CPs/MOFs),[1–3] there is considerable current interest in preparing porous crystalline frameworks using other supramolecular interactions such as hydrogen bonds, halogen bonds and chalcogen bonds. Using these weaker interactions often gives highly crystalline materials that can be prepared under very mild conditions. Of these, hydrogen bonded frameworks,[4–8] have seen the most study. While it might be thought that the weakness of the hydrogen bonding interaction would give rise to feeble frameworks, in fact surprisingly robust materials have been reported,[9–12] and hydrogen bonded frameworks have been used for a range of applications including gas sorption,[13–17] sensing[18,19] and enzyme encapsulation.[20,21] While hydrogen bonded frameworks have many advantageous properties, they have some limitations, one of which is that the relatively flexible geometry of the hydrogen bonding interaction allows the frameworks to rearrange readily, for example in response to activation under vacuum and/or guest uptake.[16,22,23]

An alternative to using hydrogen bonds to assemble frameworks would be to use "σ-hole" interactions,[24] such as halogen[25–27] or chalcogen bonding,[28,29] as these are far more directional than typical hydrogen bonds. Numerous 2D and 3D frameworks have been assembled using halogen bonding and chalcogen bonding interactions,[30–43] although perhaps surprisingly, very few permanently porous frameworks[44–46] have been reported, particularly when compared with the large number of permanently porous hydrogen bonded frameworks.

Of the many possible halogen bond donors, iodoalkynes are relatively simple to prepare and have a well-defined rod-like geometry. While some work has explored their halogen bonding with nitrogen-containing compounds,[47–49] more commonly they are used to interact with halide anions to give extended structures. Starting more than 20 years ago, Yamamoto and Kato have demonstrated that layered structures could be prepared from linear diiodoalkyne components, halide anions and tetrathiafulvalene (TTF) cations and that these had interesting charge transport properties.[50–53] More recently, the groups of Fourmigué and Bryce have demonstrated that 1,3,5-(trisiodoethynyl)-2,4,6-trifluorobenzene can form a range of halogen bonded frameworks with halide anions,[54,55] and it has been demonstrated that pyridine and pyridinium compounds containing iodoalkynes can form both discrete and extended structures.[43,56–58]

Of particular relevance to the current work, tetratopic iodoalkynes have also been used to prepare extended framework structures. Lieffrig and Yamamoto demonstrated that a tetratopic iodoalkyne based on an aryl-extended biphenyl scaffold containing activating fluorine groups could form a highly interpenetrated PtS-type network with halide anions,[59] while Aakeröy showed that a tetraphenylmethane compound with four unactivated iodoalkyne groups (*i.e.* without strongly electron-withdrawing groups) formed a highly interpenetrated diamondoid network with halides.[37] In both of these examples, the frameworks are close-packed and highly interpenetrated, and in the case of Aakeröy's diamondoid network, it was found that use of the rigid PPh_4^+ cation was necessary to obtain single crystals.

In the current work, we report the new tetratopic and hexatopic halogen bond donors **1** and **2** containing sterically-demanding methyl groups that rigidify the building blocks by restricting rotation about the phenyl–phenyl bonds (Figure 1). We demonstrate that these can be used to prepare extended 2D and 3D halogen bonded frameworks with halogen anions and a range of cations. While we have not yet been able to prepare permanently porous materials, we demonstrate that the frameworks can include large channels, accounting for almost half of the volume of the crystals.

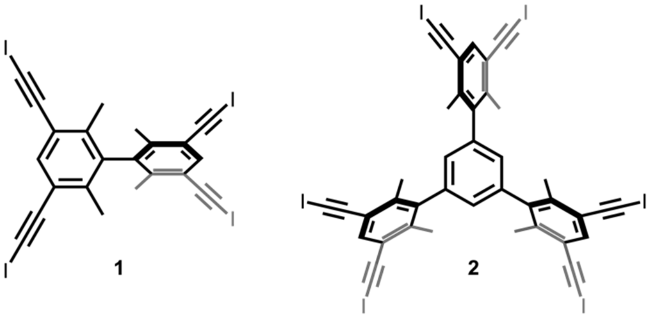

Figure 1. Tetratopic and hexatopic iodoalkynes 1 and 2 used in this work.

Results and Discussion

Synthesis of 1 and 2

The synthesis of 1 and 2 is described in the Supporting Information. Both were prepared from the corresponding alkynes by lithiation with *n*-butyl lithium and reaction with iodine. In the case of 1, the tetra-alkyne has been previously described and was readily prepared by following the literature procedure.[60] In the case of 2, the synthesis was slightly more challenging but was achieved in 35% yield over five steps starting from 1,3,5-tribromobenzene. We note Yamamoto and Kato have previously used a similar building block to 1 to prepare halogen bonded networks, however their compound does not contain the sterically-demanding methyl groups that rigidify the core of the molecule and instead contains activating fluorine groups on the biphenyl ring.[53,59] The resulting frameworks are very different to those reported here, and are densely-packed in all cases.

Synthesis of Halogen Bonded Frameworks

General Procedure: We prepared several halogen bonded networks by simply mixing solutions of 1 or 2 in dichloromethane or chloroform with TBA^+, PPh_4^+ or THA^+ salts of chloride or bromide in dichloromethane (TBA^+ = tetrabutylammonium, THA^+ = tetrahexylammonium). Upon standing, crystals formed, typically within minutes. While crystals were often large, they lost crystallinity rapidly, which we attribute to loss of solvent. In all cases, these were isolated and characterized by single crystal X-ray diffraction studies (SCXRD) and NMR spectroscopy, which confirmed the ratios of cations to receptor. We were unable to obtain useful powder X-ray diffraction (PXRD) data, which we attribute to collapse of the framework caused by solvent loss.

In some cases, SCXRD data are of limited quality due to the open structures and rapid solvent loss (see Supporting Information for more details). It was necessary to use PLATON-SQUEEZE[61] or the OLEX2 solvent mask routine[62] to account for electron density in large solvent-filled channels in all structures. In the structures of **TBA·1·Cl-3D**, **PPh_4·1·Cl** and **$TBA_{1.5}$·2·$Cl_{1.5}$**, the cations were highly disordered and so it was necessary to use PLATON-SQUEEZE or the OLEX2 solvent mask routine to include the electron density from the cation in the refinement.

Estimates of the solvent-filled void volume in the structures were made using PLATON-SQUEEZE and a sphere radius of 1.2 Å. When cations could not be modelled, their volumes were calculated using Molovol[63] (again using a radius of 1.2 Å), which gave volumes of 308 and 343 Å^3 for TBA^+ and PPh_4^+, respectively. These volumes were subtracted from the PLATON-SQUEEZE solvent-filled void (accounting for the expected number of cations based on charge-balance arguments) to allow an estimate of the solvent-filled void percentage.

Structures of TBA·1·Cl-2D and TBA·1·Cl-3D: We initially mixed a dichloromethane solution of 1 with a dichloromethane solution of TBA·Cl, and observed formation of small needle-like crystals within minutes, followed by growth of larger block-like crystals over a few days. SCXRD studies revealed the presence of two types of crystals, a 2D halogen bonded network (**TBA·1·Cl-2D**) and a three-dimensional framework (**TBA·1·Cl-3D**). Unfortunately, due to rapid solvent loss and deterioration of crystallinity upon removal from solvent, it was not possible to determine the relative ratios of crystals of the 2D and 3D frameworks.

The structure of **TBA·1·Cl-2D** is that of a corrugated sheet (Figure 2). Each chloride anion receives four halogen bonds, which range in distance from 3.121(3) – 3.140(3) Å (81% of the sum of the van der Waals radii[64] of Cl and I, Σ_{vdW}). The geometry around the chloride anion is intermediate between square planar and tetrahedral (τ_4[65] = 0.62). A TBA^+ cation sits above the anion, although there are no particularly close contacts between this cation and the anion (shortest H-Cl^- distance > 90% Σ_{vdW}). Despite the presence of charge-balancing cations, PLATON-SQUEEZE[61] analysis indicates that 47% of the unit cell is occupied by solvent-filled channels.

The structure of **TBA·1·Cl-3D** is a three dimensional framework where each chloride anion receives four halogen bonds, ranging in distance from 3.032(3) – 3.121(3) Å (79 – 81% Σ_{vdW}). The chloride anion has a geometry approximately halfway between square planar and tetrahedral (τ_4[65] = 0.56). As 1 has a tetrahedral geometry, the framework can be thought of as either a distorted diamondoid network or distorted PtS network, depending whether the anion is considered to be tetrahedral or square planar, respectively. There are two interpenetrating networks. Interestingly, this three-dimensional form of **TBA·1·Cl** contains a reduced percentage of solvent-filled voids (32%) compared with the 2D framework (47%), possibly due to the interpenetration, although this is still a substantial amount of "free" space.

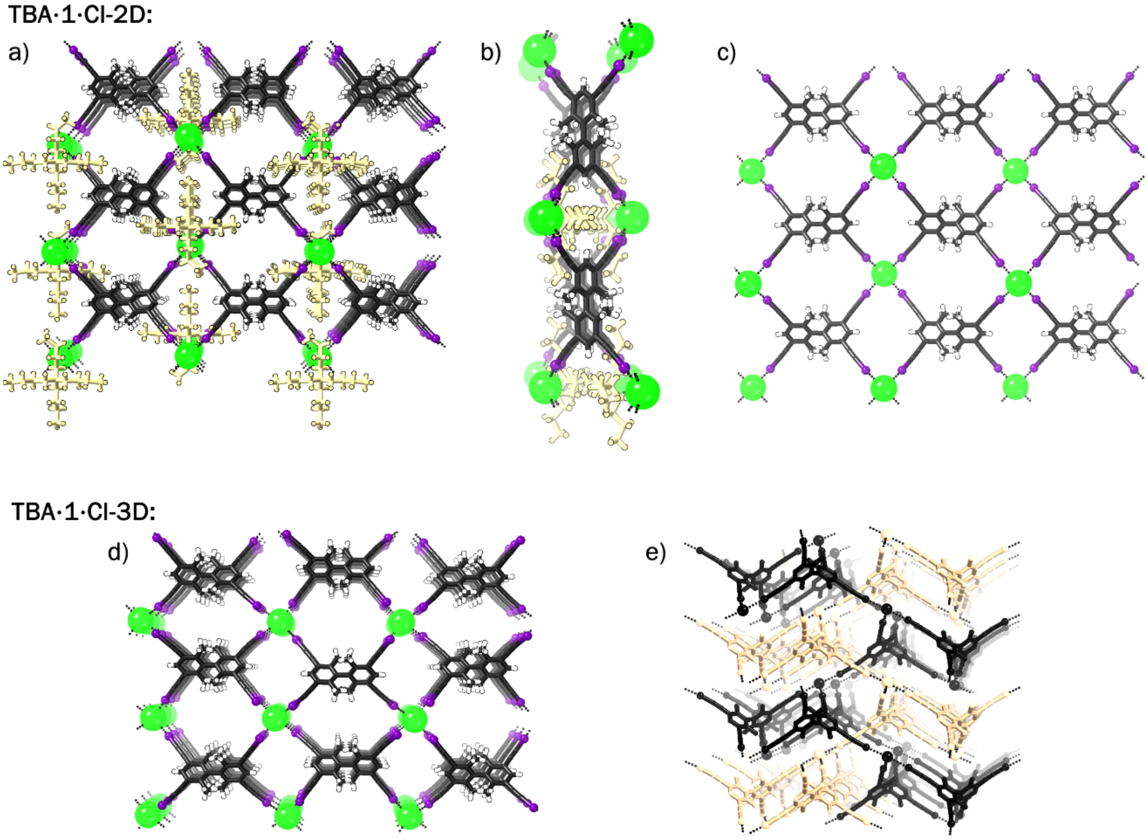

Figure 2. X-ray crystal structures of **TBA·1·Cl-2D** and **TBA·1·Cl-3D**: a) packing diagram of **TBA·1·Cl-2D**, b) view of a single layer of **TBA·1·Cl-2D** showing the positioning of the cation; c) view of a single layer of **TBA·1·Cl-2D** showing the halogen bonding arrangement (TBA$^+$ cations omitted for clarity); d) packing diagram of **TBA·1·Cl-3D** (TBA$^+$ cations could not be resolved crystallographically), e) diagram showing two interpenetrating halogen bonded lattices in the structure of **TBA·1·Cl-3D.** TBA$^+$ cations are shown in pale yellow, PLATON-SQUEEZE[61] was used in the refinement of both structures.

Effect of anion, structure of TBA·1·Br: We next investigated whether frameworks could be formed using halide anions other than chloride. When bromide was used,[66] a more concentrated solution was needed to obtain crystals, consistent with the expected weaker halogen bonds using this more charge-diffuse anion.[25] The structure of the halogen bonded network is very similar to **TBA·1·Cl-2D**, although in this case the geometry around the two crystallographically-independent bromide anions is far from either a square planar or tetrahedral geometry. The τ_4[65] parameters are 0.85 and 0.90, which are consistent with what would be expected for slightly distorted tetrahedral geometries, however the anions are clearly not tetrahedral, with all halogen bond donors sitting on one side of the anion, which perches atop a cone of iodoalkyne donors. This highlights the limits of using the τ_4 parameter (which was designed for transition metal ions) for halide anions, which have considerable geometric flexibility.

The structure of **TBA·1·Br** (Figure 3) contains slightly smaller channels than **TBA·1·Cl-2D** (43% of the unit cell of **TBA·1·Br** is made up of solvent-filled voids, compared with 47% for **TBA·1·Cl-2D**). This occurs because the 2D sheets are more corrugated, *i.e.* less flat, and thus pack slightly closer together. We note however, that this is still a surprisingly open framework given the relative weakness of the interactions used to assemble it, and the fact that the TBA$^+$ cations take up a good deal of space.

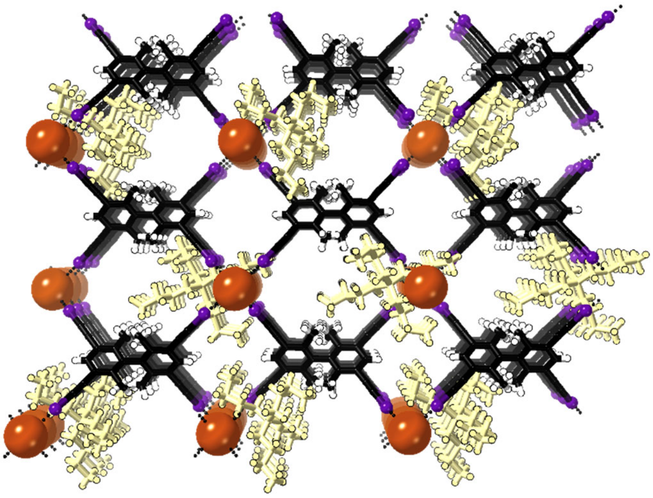

Figure 3. Packing diagram of **TBA·1·Br.** TBA$^+$ cations are shown in pale yellow, dichloromethane solvents removed for clarity. PLATON-SQUEEZE[61] was used in the refinement.

Effect of cation, structures of PPh$_4$·1·Cl and THA·1·I: Having investigated the effect of varying the halide anion, we next investigated the effect of varying the cation. Previous researchers have found that this significantly affects framework formation, and is often necessary to obtain frameworks.[37,59] However, our results using the TBA$^+$ cation indicate that frameworks containing large voids are possible using structurally rigid **1**, *i.e.* the cation is not close-packed with the halogen bonded network. We thus wondered how this would be impacted by choice of cation.[67]

Crystals of **PPh$_4$·1·Cl** were of poor quality, and unfortunately it was not possible to sensibly refine the PPh$_4^+$ cation. Nevertheless, the structure of the halogen bonded network can be unambiguously determined. The chloride anion receives four halogen bonds, which range in distance from 3.100(5) – 3.203(5) Å (80 – 83% Σ_{vdW}). The geometry about the anion is best described as somewhere between tetrahedral and trigonal pyramidal. The halogen bonded network has a pillared double-layer 2D topology (Figure 4), which is different from that of both **TBA·1·Cl-2D** and **TBA·1·Cl-3D**. Accounting for the space occupied by the PPh$_4^+$ cations, solvent-filled voids make up 47% of the unit cell.

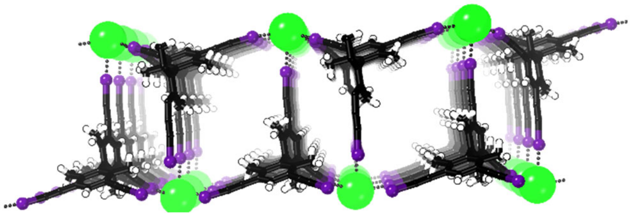

Figure 4. Packing diagram of **PPh$_4$·1·Cl** showing the double-layered 2D structure. PPh$_4^+$ cations could not be resolved crystallographically, PLATON-SQUEEZE[61] was used in the refinement.

When **1** was crystallised with tetrahexylammonium chloride (THA·Cl), the resulting crystals were found to be not **THA·1·Cl**, as expected, but instead **THA·1·I**. It is unclear where the iodide anion has come from, it could be either an impurity present in the commercial source of THA·Cl, or the result of decomposition of **1** resulting in free iodide and presumably the proto-alkyne. While no evidence of the proto-alkyne was observed in the ^{1}H NMR spectrum of the isolated crystals, it is possible that a small amount of this forms and stays in solution during crystallisation (crystals of **THA·1·X** where X = Cl$^-$/I$^-$ were isolated in ~ 40% yield, see SI). Unfortunately, due to the difficulty in obtaining quality X-ray diffraction data caused by crystals rapidly solvent, we were unable to determine the X-ray crystal structure of **THA·1·Cl**.

The structure of **THA·1·I** has a 2D corrugated sheet-like structure. The iodide anion receives four halogen bonds, with **I**···I$^-$ distances ranging from 3.436(2) – 3.573(2) Å (84 – 88% Σ_{vdW}). As was the case in the related 2D structure of **TBA·1·Br**, the anion perches atop a cone of halogen bond donors. Interestingly, despite the larger cation, the unit cell volume per molecule of **1** is smaller than in any of the structures. That is, rather than the larger cation templating a bigger framework, it in fact results in a (slightly) smaller network. This, coupled with the large size of the THA$^+$ cation results in solvent-filled voids that make up only 13% of the unit cell volume, much smaller than the 32 – 47% observed in the other networks formed from **1**. Additionally, the voids no longer form connected channels.

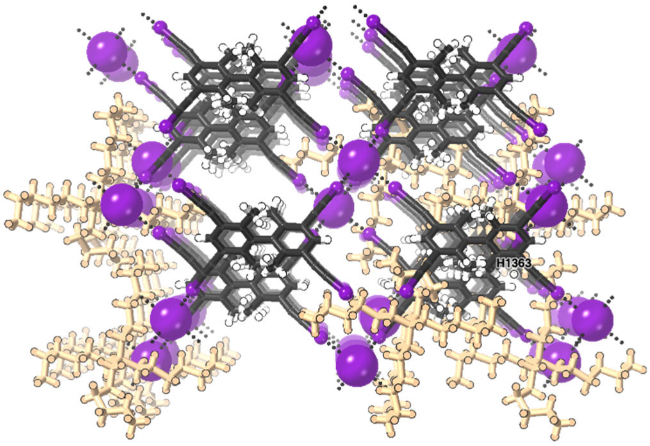

Figure 5. Packing diagram of **THA·1·I**. THA$^+$ cations are coloured peach, dichloromethane solvents removed for clarity. PLATON-SQUEEZE[61] was used in the refinement.

TBA$_{1.5}$·2·Cl$_{1.5}$: Having demonstrated that a range of open structures could be prepared from **1** and halide anions, we next turned our attention to the potentially hexatopic halogen bond donor **2**. Unfortunately, the low solubility of **2** made obtaining crystals challenging. However, crystallising this with TBA·Cl gave the halogen bonded framework **TBA$_{1.5}$·2·Cl$_{1.5}$**, which contains 1.5 chloride anions per molecule of **2**. The anions each receive four halogen bonds, which range in distance from 3.072(2) to 3.151(2) Å (80 – 82% Σ_{vdW}). The chlorides have approximately square planar geometries (τ_4[65] parameters 0.03 and 0.38), while the TBA$^+$ cations could not be resolved crystallographically and so were included in the model using the OLEX2 mask routine.[62] Accounting for the TBA$^+$ cations that could not be resolved crystallographically, 40% of the unit cell is made up of solvent-filled channels.

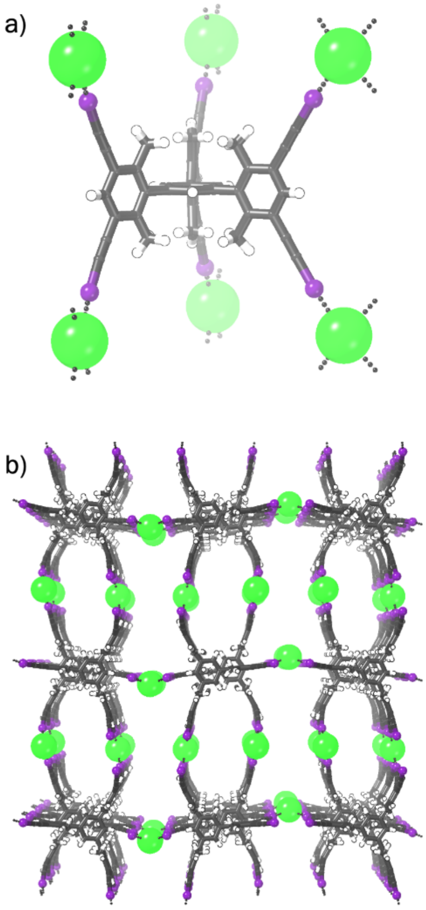

Figure 6. X-ray crystal structure of **$TBA_{1.5}$·2·$Cl_{1.5}$**: a) view of the halogen bonding around one molecule of **2**; b) packing diagram. TBA^+ cations could not be resolved crystallographically, OLEX2 solvent mask[62] was used in the refinement.

Role of the arylene methyl groups: The notable void space in the structures of **1** appears to be driven in part by the 2,2',6,6'-tetramethyl groups, which limit the rotational freedom of the biphenyl backbone through steric hinderance. As a result, the phenyl–phenyl mean plane angles approach 90° (range 78.4 – 87.5°), and the four iodoalkyne donors adopt a pseudo-tetrahedral geometry. These angles are significantly closer to 90° than the related tetraiodoacetylene–biphenyl compounds prepared by Yamamoto and Kato,[53] and Lieffrig and Yamamoto[59] bearing smaller fluoro groups at the 2,2' and 6,6' positions, which sit notably flatter, with mean plane angles of 52.7° and 66.2°, respectively. A small amount of flexibility in the mean plane angles remains, however. Interestingly, the mean plane angles in the series of 2D corrugated structures increase with increasing anion size (78.4°, 84.7° and 87.5° for **TBA·1·Cl-2D**, **TBA·1·Br** and **THA·1·I**, respectively). It appears that the final angle and thus the depth of the corrugations may be influenced by the anion, with increasing anion radius and I-X^- bond length seeing a reduction in the depth of the layers.

Conclusions

This work demonstrates that iodoalkyne–halide interactions can be used to prepare halogen bonded frameworks containing significant amounts of solvent-filled void space. The interaction is relatively predictable in that all systems apart from that containing the very large THA^+ cation contained large amounts of void space (32 – 47% of the unit cell volume). However, it is simultaneously unpredictable in that a range of framework topologies are observed from very starting materials, *e.g.* **1** and Cl^- gave 2D, 3D and pillared networks with TBA^+ or PPh_4^+ cations. This appears to be related in part to the significant variability in the coordination geometry of the halide anions with arrangements of halogen bonds ranging from approximately square planar to tetrahedral, trigonal pyramidal and conic observed.

Often in these kinds of “anion-templated” crystal engineering studies, the cation is critical in determining the nature of the product as it packs tightly with the growing framework.[37,68,69] However, in the current work there is significant void space, even accounting for the large cations, *i.e.* the framework does not grow tightly around the cation. While in the current work, the frameworks lose crystallinity upon drying, it builds on previous work, which found that networks formed from tetratopic iodoalkynes tended to only form close-packed frameworks.[37,53,59] It appears that rigidifying the halogen bond donor molecules by the use of sterically-demanding groups increases the propensity for highly open structures. We suggest that these types of frameworks are promising candidates for future permanently porous materials, particularly if ways to incorporate the cations into the framework can be found.

Supporting Information

The authors have cited additional references within the Supporting Information.[71–78]

Deposition Numbers 2335610 (for **TBA·1·Cl-2D**), 2335611 (for **TBA·1·Br**), 2335612 (for **PPh_4·1·Cl**), 2335613 (for **TBA·1·Cl-3D**), 2335614 (for **THA·1·I**) and 2335615 (for **$TBA_{1.5}$·2·$Cl_{1.5}$**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe.

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