

Porous isorecticular non-metal organic frameworks

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Metal-organic frameworks (MOFs) are useful synthetic materials that are built by the programmed assembly of metal nodes and organic linkers¹. The success of MOFs results from the isorecticular principle², which allows families of structurally analogous frameworks to be built in a predictable way. This relies on directional coordinate covalent bonding to define the framework geometry. However, isorecticular strategies do not translate to other common crystalline solids, such as organic salts³⁻⁵, where the intermolecular ionic bonding is less directional. Here we show that chemical knowledge can be combined with computational crystal structure prediction⁶ to design porous organic ammonium halide salts that contain no metals. The nodes in these salt frameworks are tightly-packed ionic clusters that direct the materials to crystallize in specific ways, as evidenced by well-defined spikes of low-energy, low-density isorecticular structures on the predicted lattice energy landscapes^{7,8}. These energy landscapes allow us to select combinations of cations and anions that will form thermodynamically stable porous salt frameworks with channel sizes, functionalities, and geometries that can be predicted *a priori*. Some of these porous salts absorb guests such as iodine in quantities that exceed most MOFs, which could be useful for applications such as radioiodine capture⁹⁻¹². More generally, the synthesis of these salts is scalable, involving simple acid-base neutralisation, and the strategy opens up a family of non-metal organic frameworks combining high ionic charge density with permanent porosity.

Porous crystalline solids are interesting both for their fundamental chemistry and their potential in applications such as gas capture, catalysis, and molecular separations. The ability to position chemical functionality with atomic precision in crystalline porous frameworks has created properties that do not

exist in classical porous materials, such as activated carbons. Porous crystalline solids can be divided into two classes: extended, covalently-bonded frameworks, such as metal-organic frameworks (MOFs)^{1,2} and covalent-organic frameworks (COFs)^{13,14}, and porous molecular crystals, such as hydrogen-bonded frameworks (HOFs)^{7,8,15,16} and porous organic cages (POCs)¹⁷. Porous bonded frameworks exploit strong, directional covalent or coordinate covalent bonding, which underpins the isorecticular principle², whereby series of structurally related frameworks can be synthesized. By contrast, porous molecular crystals involve weaker, non-covalent intermolecular interactions. Hence, they are harder to design for a specific, programmed function, and less amenable to generalization.

Crystalline porous organic salts (CPOS)⁵ are a sub-class of porous molecular solids that are composed of acids and bases assembled through ionic interactions. Ward and colleagues^{3,4} pioneered this area in the early 1990's, before the first porous MOFs were discovered^{18,19}. However, while MOFs have since burgeoned, CPOS materials have not had the same success. MOFs have the advantages of reticular design, high levels of permanent porosity and, in some cases, good physicochemical stability. By contrast, while porous salts show promise for some applications^{5,20,21}, they lack many of the basic design principles that apply to isorecticular frameworks. For example, porous molecular salts can be subject to polymorphism²² because the interactions between net charges in organic salts are less directional than coordinate covalent bonding in MOFs.

The potential for polymorphism in neutral HOFs has been tackled by using *a priori* crystal structure prediction (CSP)^{7,8} to map the landscape of stable crystal packing modes and, hence, to predict the resulting physical properties. The area of MOFs has also seen recent developments in CSP^{23,24} that could be used to anticipate likely stable structures for particular metal-linker combinations; the covalent bonding between metal nodes and organic linkers requires periodic density functional theory to adequately describe the relative energies of alternative structures, unlike organic molecular CSP where intermolecular force fields can often capture the balance between competing non-bonded interactions. This makes structure-searching much more expensive in MOF CSP and, so, these studies have made heavy use of symmetry to guide the placement of MOF building blocks during random structure searching to reduce computational expense.

To date, CSP has not been applied to CPOS materials. Moreover, CSP has only rarely been applied to organic salts^{6,25,26} because of the challenges in modelling the range of interactions governing their structure, conformational flexibility in the building blocks, and the high dimensionality of the energy landscape that results from having multiple independent units in the crystallographic asymmetric unit.

Recent advances in the crystal engineering of porous organic salts and related systems have shown that some directionality can be forced in salts by using nonpolar steric hindrance around the charged sites²⁷, but those materials were not porous. A level of reticular chemistry was made possible by using carboxylic acids and amidines²⁸, but this strategy is less generalizable than isorecticular MOFs. Again,

those amidine salts were not activated successfully to yield porous structures. Brekalo *et al.* showed that guanidinium organodisulfonates, while formally metastable with respect to dense packings, can retain microporosity for extended periods.²⁹ More broadly, Yu *et al.* reviewed CPOS materials in 2020 and concluded that “Most crystalline porous organic salts formed by noncovalent bonding remain unstable, leading to collapse of the framework after removing the guest molecules”⁵. Compared with MOFs, there are very few ‘porous organic salts’, and the majority of those reported are not, in fact, permanently porous.

While permanently porous organic salts have proved challenging to design, they retain a conceptual and practical allure. For example, a wide range of salt-forming reactions exists as a toolkit for forming porous salts, making them potentially analogous to ‘MOFs without the metals’. Also, one might expect to find unique physical properties in all-organic porous salt frameworks that have a high density of permanent charges lining the pores.

Ammonium halides are an archetypal class of organic salts that are widely studied in pharmaceutical chemistry, making up a significant percentage of drug molecules. However, in the area of porous frameworks they are largely unexplored. White and co-workers reported densely packed ammonium salts^{30,31} and showed that some have the ability to capture sulfate ions³². Feng *et al.* reported a different dense ammonium salt that could efficiently catalyze the reduction of U(IV) to U(VI)³³. Also, while this manuscript was being written, Xie *et al.* reported porous ammonium halide salts that could adsorb gases such as krypton and xenon³⁴, although those materials were synthesised without any computational structural design.

We show here that ammonium halide salts can form porous, thermodynamically-stable frameworks that can be targeted by using *a priori* CSP. We also demonstrate that these porous salts can form predictable, isorecticular structure families, as for MOFs^{1,2,33} and COFs³⁵. For example, we show that isorecticular forms persist across compound families if the length of the amine linkers is extended. These porous salts show robust, desolvatable porosity and exhibit useful properties such as high levels of iodine capture⁹⁻¹².

Reticular design principle

Typically, MOFs consist of positively charged metal nodes connected by negatively charged organic linkers¹⁸ (Figure 1a), or neutral coordinating linkers with counteranions to balance the charge¹⁹. An inverse approach is to construct frameworks where negatively charged nodes are connected by positively charged linkers (Figure 1a). Our basic design principle was to use rigid organic linkers bearing multiple amine groups (Figure 1b). We imagined that crystals of the halide salts of these linkers would necessarily pack such that the cations and anions were in close proximity, and that this clustering of the salt functionality, coupled with the rigidity and length of the linkers, might lead to permanent

porosity. Beyond this simple mental picture, though, it was impossible to anticipate the precise packing in such crystals because of the lack of strong directional intermolecular bonding in ammonium halide salts. For this reason, we applied CSP to explore the likely low-energy packing modes for these salts prior to synthesis.

Crystal structure prediction to guide synthesis

First we explored a tetrahedral amine linker, TAPM (Figure 1b). The energy-structure landscapes derived from CSP calculations for the hypothetical chloride and bromide salts of TAPM are shown in Extended Data Fig. 1. In both cases, the lowest energy structures were predicted to be dense and non-porous, suggesting that TAPM was not a promising candidate for stable, permanently porous CPOS materials, at least with halide counterions, even though structurally analogous anionic tetrahedral sulfonates were used previously to create porous salts⁵. To test this predicted outcome, single crystals of tetrakis(4-aminophenyl)methane.X (X = Cl, Br) (**TAPM.X**) were grown by reacting TAPM with either HCl or HBr. By exploring a range of crystallization conditions, we found that two polymorphs, **TAPM.X/P1** and **TAPM.X/P2**, can be formed and these polymorphs are isostructural for both halides. CSP finds structures with the experimental crystal packings observed in the two polymorphic forms for both TAPM salts (Extended Data Fig. 1c,d). As predicted, both **TAPM.X/P1** and **TAPM.X/P2** are dense and non-porous. **TAPM.X/P1** was identified as the lower-energy structure on both CSP landscapes (Extended Data Fig. 1a,b) and it was found to be the dominant form, produced under most crystallization conditions. While these two salts did not yield porous frameworks, the results gave us confidence in the CSP methodology for these challenging systems, where the calculations involved five independent structural units; that is, the TAPM tetracation and four halide anions.

Next, CSP calculations were performed on a wider range of amines and halides to search for candidate porous salt frameworks. The predicted structural landscapes for three promising candidate salts are shown in Figure 2a-c, all of which involve trigonal, triamine linkers. For each of these salts, the lowest energy predicted structures have pore channels that would be large enough to accommodate guests. Moreover, the energy-density distributions of predicted crystal structures show pronounced ‘spikes’ containing multiple porous crystal packings that are broadly isostructural. Such features of CSP landscapes were shown previously for neutral HOFs^{7,8,37} to correspond to deep, isolated basins on the lattice energy surface³⁸ and this is most obvious in the energy-density distributions for **TT.Br** and **TTBT.Cl**. For **TAPT.Cl**, the additional structural dimension of cation flexibility obscures similar spikes in the overall energy-density distribution (TAPT-1,2 and 4 in Figure 2a); nevertheless, spikes formed by some cation conformers are expected to correspond to isolated, deep basins on the combined intramolecular-intermolecular energy surface. The prediction of global energy minimum porous structures for these salts contrasts sharply with the porous metastable polymorphs that we predicted for neutral HOFs, which had lattice energies that were up to 50 kJ mol⁻¹ above the predicted close-packed

crystal structures^{7,8,37}. This provides an insight that organic salts might be more suitable for creating intrinsic porosity, which is important for applications because metastable crystals are subject to porosity loss by densification.²⁹

The CSP calculations also showed that this series of salts might be isorecticular, as for MOFs². That is, the linker with the longest arms, **TTBT**, was predicted to yield salts with crystal packings that are isorecticular with salts of the short-arm linkers, **TT** and **TATP**, but with larger pore channels and a higher pore volume (*c.f.*, Figure 2e and 2f).

Synthesis of porous salts

Bulk crystalline powders of **TAPT.Cl**, **TT.Br** and **TTBT.Cl** were isolated through simple dropwise addition of either HCl or HBr solutions into solutions of the respective amines, whereby the salts precipitated instantaneously. Structural matches for the three isolated salts could be found on their CSP landscapes by comparing predicted and experimental PXRD patterns (Figure 2g-i), as indicated by the red stars in Figure 2a-c. In all three cases, these matches were found to lie at the tip of a ‘spike’ in the CSP landscape, and for **TT.Br** and **TTBT.Cl** these structures corresponded to the predicted global energy minimum structures.

The three predicted crystal packings that best matched the experimental data were all isorecticular and comprised two distinct one-dimensional (1-D) pore channels, as labelled in Figure 2d-f. The first pore (A) is defined by clusters or ‘tubes’ of the protonated amines and the halide counterions; it is cylindrical, highly charged, and has a narrow pore diameter (4.86–5.87 Å). The second pore (B) is roughly diamond in shape, less polar, and defined by the aromatic linkers; this pore diameter is significantly larger in **TTBT.Cl** (14.3 Å × 8.5 Å) than in **TAPT.Cl** (7.9 Å × 4.6 Å) or **TT.Br** (7.0 Å × 5.8 Å), while the dimensions of the ionic pore (A) are almost the same in all three predicted structures. This dual channel structure leads to predicted pore volumes in these trigonal amine salts that are higher than for 4,4',4'',4'''-(ethene-1,1,2,2-tetrayl)tetraaniline (ETTA) salts³⁴. For example, using a probe radius of 1.2 Å, the calculated solvent accessible pore volume for **TATP.Cl** is 31.9% of the unit cell volume, 31.4% for **TT.Br**, and 43.2% for the larger-pore isorecticular framework, **TTBT.Cl**. The equivalent calculated pore volume calculated for the chloride salt of ETTA (**ETTA.Cl**) is 18.2%³⁴. This four-arm linker, ETTA, is closer in structure and geometry to TAPM (Figure 1b), which gives dense, non-porous salts here (Extended Data Fig. 1).

Single crystals of **TAPT.Cl** grown from methanol and chlorobenzene revealed that the salt crystallized in a trigonal space group, *P3m1* (Supplementary Fig. S6). This experimental crystal structure, albeit for a partial solvate (**TAPT.Cl**, 1.25[C₆H₅Cl], 1.5[H₂O]), confirmed the match for the computationally predicted structure. In this solvate, the solvent occupies around 78% of the void volume. A structural overlay of the predicted and experimental structure is shown in Extended Data Figure 2b. This is the

first experimental evidence that organic salts can form porous frameworks that follow an *a priori* atomistic structure prediction.

Crystals also formed for both **TT.Br** and **TTBT.Cl**, but the lower solubility and higher reactivity of those systems meant that publishable single crystal X-ray data could not be obtained. Conversely, this high reactivity and low solubility allowed us to obtain multiple grams of (poly)crystalline powders for these materials within hours by simple dropwise addition of acid at room-temperature (see Methods section). Comparison of experimental powder X-ray diffraction data with equivalent data derived from the global energy minimum CSP structures (Figure 2h,i) suggested that **TT.Br** and **TTBT.Cl** formed crystal packings that were broadly isorecticular: that is, extension of the organic linkers led to larger pores, as for isorecticular MOFs. Given the challenges in growing single crystals, high resolution transmission electron microscopy (HR-TEM) was used to further characterize these materials, as used to provide structural information for other porous frameworks^{39,40}. HR-TEM further demonstrates the crystallinity of **TT.Br** and **TTBT.Cl** (Extended Data Fig. 3a,b). The highly crystalline structure of **TT.Br** is shown in Extended Data Fig. 3a, where the inset shows an expansion of the rectangle in the middle of the particle, showing the anticipated pore structure. To further confirm the proposed crystal packing of **TT.Br**, we compared the Fast Fourier Transform (FFT) of the experimental HR-TEM (Extended Data Fig. 3a, top right) with the simulated electron diffraction pattern for the best-matched CSP structure (Extended Data Fig. 2a, bottom right). The yellow and blue dashed circles in both patterns correspond to the first and second hexagonal order, with d-spacing values of 1.572 nm and 0.92 nm, respectively. For **TTBT.Cl** (Extended Data Fig. 3b), HR-TEM shows the 1-D pore channels in the crystal and the corresponding FFT image (Extended Data Fig. 3b, top right) shows the (010), (020) and (030) axes with an alignment along the [010] zone axis determined after comparison with the simulated pattern from the best-matched CSP-derived structure (Extended Data Fig. 3b, bottom right). The halos observed in the FFT images suggest that there is uncorrelated disorder in these two materials, particularly for **TTBT.Cl** (Extended Data Fig. 3b). The crystal structure of **TTBT.Cl** was solved using PXRD data (Extended Data Fig. 3c). All of these data support the structure assignments made in Figure 2.

Ionic interactions create porosity

Analysis of the CSP energy landscapes reveals that our initial design hypothesis of charge adjacency was satisfied, at least for the three trigonal amine linkers. Figure 3 summarises the anion coordination of the ammonium groups, presented as the mean count of nitrogen-halide close contacts per ammonium in each predicted crystal structure. Low density spikes of structures correspond to maximization of such close contacts, reaching an average of four close halides per ammonium in the most stable porous structures. That is, porosity arises from the crystal packing constraints introduced by closely adjacent net charges attached to rigid aromatic linkers. The trigonal organic linkers express this charge adjacency

more effectively than the two tetrahedral salts. For **TAPM.Cl** and **TAPM.Br**, there are no low-energy crystal structures predicted that allow more than three close contacts between the ammonium nitrogen atoms in the organic linkers and the halide nodes (Figure 3a,b). This means that the electrostatic interactions do not overrule the stabilisation that can be achieved by close packing. Hence, these salts do not form open porous frameworks. By contrast, the trigonal amine linkers **TT.Br** and **TTBT.Cl** yield CSP landscapes containing structures with four close halide contacts per ammonium nitrogen (Figure 3d,e); these structures predominate in the ‘spikes’ of low-energy, low-density predicted packings. The **TT.Br** and **TTBT.Cl** energy landscapes show clearly why an open, low-density structure is formed: structures with higher densities form fewer ammonium-halide close contacts and are therefore less energetically stable. For **TAPT.Cl**, the predicted crystal packing that corresponds to experiment has three close chloride contacts per ammonium according to the distance thresholds in Figure 3. However, the number of close contacts is sensitive to the threshold value, and for **TAPT.Cl** it increases to four chloride close contacts around two of the cation’s arms with a 25% increase in the distance cutoff (Supplementary Fig. S34). For all three trigonal amine salts (Figure 2d-f), the packing arrangement with four close halide-ammonium contacts is expressed by the cylindrical ionic pores (A) (Figure 3f), which in turn create the diamond-shaped pores (B).

Other potential porous polymorphs

As found for neutral HOFs^{7,8,37}, these CSP landscapes suggest that other porous polymorphs might also be accessible in the laboratory (Extended Data Fig. 4–6). For example, alternative porous structures were predicted for **TATP.Cl**, some of which had lower predicted lattice energies than the experimentally observed crystal packing (*e.g.*, **TAPT.Cl/4** and **TAPT.Cl/5** in Extended Data Fig. 4), at least in the absence of solvent. We also predicted structures with significantly higher pore volumes, such as **TAPT.Cl/3** (Extended Data Fig. 4), which lies 29.7 kJ mol⁻¹ above the global minimum. By analogy with HOFs, where solvent stabilization of at least 50 kJ mol⁻¹ has been observed for porous polymorphs^{7,8,37}, **TAPT.Cl/3** or a nearby structure in the predicted set could in principle be accessible under different experimental conditions. Likewise, the CSP landscapes for **TT.Br** (Extended Data Fig. 5) and **TTBT.Cl** (Extended Data Fig. 6) suggest other potential porous forms within a relative lattice energy window of 50 kJ mol⁻¹, although in these two cases, the experimentally observed polymorphs match the global minimum energy predicted structures (Figure 2b,c). Closely related crystalline forms can be found across the three energy landscapes: for example, **TT.Br/4** and **TTBT.Cl/3** are isorecticular with **TAPT.Cl/3** (Extended Data Fig. 7). Likewise, **TAPT.Cl/2**, **TT.Br/1** and **TTBT.Cl/1** are all isorecticular (albeit with high relative lattice energies), as are structures **TT.Br/5** and **TTBT.Cl/4**, and structures **TAPT.Cl/4** and **TT.Br/6**, which have more competitive predicted lattice energies.

We can also use energy-structure-function (ESF) maps⁷ to predict global property tendencies. For example, the dominance of red datapoints in ESF maps coloured by pore channel dimensionality (Extended Data Fig. 8a–c) shows that all three of these salts would be expected to express 1-D channel geometries, rather than 2-D or 3-D channels, if a porous structure is formed. Likewise, ESF maps suggest that **TTBT.Cl** has the greatest chance of forming a mesoporous structure with pores larger than 2 nm in diameter (Extended Data Fig. 8d–f), such as **TTBT.Cl/3**, although only microporous materials (pores < 2 nm) were observed under the experimental conditions tested here.

Gas sorption in porous salts

These materials did not adsorb significant quantities of nitrogen at 77 K, but this is relatively common for small-pore microporous solids and may reflect limited guest mobility at those temperatures. By contrast, all three porous salts absorbed carbon dioxide reversibly at temperatures in the range 195 K–298 K (Extended Data Fig. 9). **TAPT.Cl** and **TT.Br** absorb 4.0 and 4.6 mmol g⁻¹ CO₂, respectively, at 195 K as saturation is approached. **TT.Br** in particular absorbs more CO₂ than other porous organic salts at this temperature^{5,34,41,42}. By contrast, **TTBT.Cl** absorbed around 2.4 mmol g⁻¹ despite having the lowest predicted crystal density and the largest nominal pore volume (Figure 2). The CO₂ desorption isotherm for **TTBT.Cl** at this temperature also shows pronounced hysteresis, unlike **TAPT.Cl** and **TT.Br**, and the isotherm collection time was long (>90 h). It is likely that the low-density **TTBT.Cl** crystals are less stable to the degassing conditions used here (14 h at either 80 °C or 110 °C), and hence some porosity is lost upon sample preparation or during sorption and desorption (Supplementary Fig. S14). By contrast, as discussed below, **TTBT.Cl** exhibits the highest capacity, good stability, and the most rapid absorption kinetics for guests such as iodine when activated under less rigorous conditions. Unlike the CO₂ isotherms, this supports our prediction that **TTBT.Cl** should have the highest pore volume in this isoreticular series of porous salts.

Porous salts for iodine capture

The capture of radioiodine is important in the nuclear industry and for environmental protection^{9-12,43}. These salts with their highly polar pore channels struck us as potentially useful adsorbents for iodine capture. Non-porous **TAPM.Cl_P1** showed very little iodine uptake (3.6 wt.%, Figure 4a), which was ascribed to adsorption on the crystal surface. By contrast, the three porous salts, **TAPT.Cl**, **TT.Br** and **TTBT.Cl** showed high iodine uptakes of 248 wt. % (6.8 mol/mol), 213 wt. % (4.99 mol/mol) and 211 wt. % (3.83 mol/mol), respectively. These iodine uptakes outperform most MOFs studied at comparable temperatures (60–80 °C), including ZIF-8 (125 wt. % iodine),⁹ Cu-BTC (175 wt. %)¹⁰, MFM-300(Sc) (154 wt. %)¹¹, and NU-1000 (145 wt. %)¹². Indeed, a recent review⁴³ suggests that **TTBT.Cl** adsorbs more iodine than all but five MOFs reported, all of which have high surface areas (>2000 m² g⁻¹) and lower framework densities than this non-metal organic framework. Moreover, the iodine uptake in these salt frameworks is reversible over multiple cycles (Figure 4c,d).

Water stability

The stability of frameworks to water is another important practical consideration. For these ammonium halide salts, this depends on the organic linker. **TAPT.Cl** is water soluble while **TT.Br** has very low water solubility, but becomes amorphous upon immersion in water. By contrast, the more hydrophobic **TTBT.Cl** framework is insoluble in water and a sample submerged in water was shown by PXRD to have stable crystallinity for at least 48 h (Supplementary Fig. S23). Water adsorption isotherms were also collected for **TTBT.Cl** and it was shown to adsorb 12.4 mmol g⁻¹ of water (Supplementary Fig. S24). PXRD analysis before and after water sorption showed that the sample had retained a good level of crystallinity.

Outlook

In this study, we have introduced a computational design-led strategy for non-metal containing framework materials. The frameworks can be produced on multigram scales from earth abundant elements by simple dropwise addition of acid to solutions of the amine linkers. The first examples of these materials already show practical promise, outperforming most MOFs for iodine capture⁴³. Other applications can be envisaged that might take advantage of the highly charged pore channels (Figure 2, Figure 3f), such as proton conduction, catalysis, water capture, or hydrogen storage.

These frameworks can be thought of as ‘inverted’ MOFs, where the halide anions are analogous to the metal cations (Figure 1a); that is, non-metal organic frameworks. Just as MOFs can be structurally diversified by changing the metal nodes and the organic linkers, it should be possible to create similar families of non-metal organic frameworks. We chose ammonium halides here because they are easy to synthesize and well known in a pharmaceutical context, but this inverse reticular strategy should be diversifiable. For example, a wide variety of other counterions can be considered such as nitrates, sulfates, tetrafluoroborates, hydrogen carbonates, phosphates, cyclic phosphates, arsenates, carboxylates, and tetrafluoroborates, to name but a few, all of which are known to form salts with ammonium cations. Mixed anion frameworks are also possible³⁴, although predicting the most stable salt composition *a priori* could be computationally expensive. Just as for MOFs, a range of organic amine linkers can be conceived, including aliphatic amines, providing that they are sufficiently rigid, as well as pyridinium or imidazolium analogues.

Like MOFs, but unlike other covalent non-metal frameworks, such as COFs^{13,14}, these materials are synthesized by salt formation. This is reversible enough to produce single crystalline materials (Supplementary Fig. 6), which is still relatively uncommon for COFs⁴⁴⁻⁴⁸. These molecular salts also have properties that are not found in bonded frameworks such as solubility in certain solvents (Supplementary Figs. 5,7,10), which may aid processing and purification.

We observed polymorphism for **TAPM.X** salts (Extended Data Fig. 1), and CSP calculations suggest that other ammonium halide salts might in principle be polymorphic, too (Extended Data Figs. 4–6), although CSP is known to overpredict polymorphism^{49,50}. Interestingly, polymorphism has not been observed in crystalline guanidinium organosulfonate materials^{3,4,29}. This might be due to more directional hydrogen bonding between guanidinium ions and sulfonate groups restricting the possibilities for low energy crystal packings, in comparison with ammonium halide salts that comprise simple spherical anions. This could have broader implications for the design of non-metal organic frameworks using anions other than halides.

We see CSP as the key to exploring this area because the ionic bonding in these salts is weaker and less directional than for most MOFs, and CSP allows us to evaluate the propensity for new combinations of organic cations and counterions to form stable, porous crystals prior to synthesis. This will identify candidates for porous frameworks from the much larger pool of organic salts that form dense, non-porous crystals, or that cannot be activated because they are metastable⁵. Moreover, the ability to predict frameworks that have thermodynamically stable porous forms is a major advantage for applications. The robust porosity in **TTBT.Cl** and its stability to multiple iodine sorption-desorption cycles (Figure 4c) can be explained by the absence of denser, more stable packings available to this crystal (Figure 2c). This is not the case for most hydrogen-bonded organic frameworks, nor indeed for many MOFs. For example, our earlier neutral porous HOFs⁷ may be unsuitable for iodine capture applications because there are multiple, denser polymorphs available that are more stable, and the porosity would be lost under practical capture conditions.

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Figure 1. Inverse reticular design strategy for porous salt frameworks. **a**, Most MOFs comprise positively charged metal nodes (M^{n+}) and negatively charged organic ligands (L^{m-}). An inverse strategy is to design organic salt frameworks with negatively charged nodes (X^{n-}) and positively charged organic linkers (L^{m+}). **b**, Structures of the aniline derivatives used as linkers. TAPM: tetrakis-(4-aminophenyl)methane; TAPT: 1,3,5-tris(4-aminophenyl)benzene; TT: 4,4',4''-(1,3,5-triazine-2,4,6-triyl)tris[benzenamine]; TTBT: 4',4''',4''''-(1,3,5-triazine-2,4,6-triyl)tris[[1,1'-biphenyl]-4-amine]. These linkers take the form of cationic ammonium halide salts in the resulting salt frameworks.

Figure 2. Crystal structure prediction suggests porous, isorecticular ammonium halide salts. **a–c**, CSP energy landscapes for **a**, TAPT.Cl, **b**, TT.Br and **c**, TTBT.Cl. For TAPT and TTBT, we considered the four lowest energy molecular conformers predicted for the amine linker, and these are colour-coded in the CSP landscapes. TT was assumed to adopt a planar confirmation (the computed minimum energy conformer) because of its triazine core. We carried out CSP for both the chloride and bromide salts for all three systems; the TT.Br landscape is shown here because this salt crystallized more effectively than the corresponding chloride. For all three salts, the lowest energy, most thermodynamically stable structures are predicted to be porous. **d–f**, Space-filling representations of the closest CSP matches (red stars in **a–c**) found for the observed experimental structures of **d**, TAPT.Cl, **e**, TT.Br and **f**, TTBT.Cl. For TT.Br and TTBT.Cl, the closest matches are the global minimum energy structures. **g–h**, Comparison of experimental powder X-ray diffraction (PXRD) data (black) with PXRD pattern predicted from closest match in CSP landscape (red) for **g**, TAPT.Cl, **h**, TT.Br and

i, TTBT.Cl. Details of the analyses for **TAPT.Cl** and **TT.Br**, and the refinement for **TTBT.Cl** are given in the Supplementary Information (Section 2).

Figure 3. Charge adjacency dictates crystal packing. CSP plots colour coded by the mean number of short contacts (below the sum of nitrogen and halide van der Waals radii, 3.3 Å for chloride salts, 3.4 Å for bromide salts) between ammonium nitrogens and the halide ions for **a, TAPM.Br**, **b, TAPM.Cl**, **c, TAPT.Cl**, **d, TT.Br** and **e, TTBT.Cl**. Experimentally observed dominant polymorphs are indicated by a star. **f**, Global energy minimum predicted structure for **TTBT.Cl** emphasising the four short ammonium–halide contacts (dotted lines) that define the cylindrical pore channel (A) in Fig. 2f; purple atoms are the nitrogen atoms in the NH_3^+ cation (hydrogens not shown); green atoms are Cl^- anions.

Figure 4. Reversible iodine uptake in porous organic salts. **a**, Plot showing the iodine uptake in porous **TAPT.Cl**, **TT.Br**, and **TTBT.Cl** frameworks and non-porous **TAPM.Cl_P1** as a function of time. Note that the **TAPT.Cl** and **TT.Br** plots overlay almost exactly. **b**, Photographs of the salts before and after exposure to iodine; **c**, Recyclability tests over 5 cycles for **TTBT.Cl**, where 100% efficiency is defined as the initial iodide uptake (cycle 1). **d**, PXRD data showing reversibility of iodine adsorption in **TTBT.Cl**; comparable reversibility was observed for **TAPT.Cl** and **TT.Br**, see Supplementary Figs. 20,21.

Methods

Crystal structure prediction

Two of the four amines studied, **TAPM** and **TT**, have only one predicted conformer (Supplementary Fig. 25). By contrast, **TAPT** and **TTBT** each have four predicted low-energy conformers (Supplementary Figs. 26,27). These molecular structures were obtained by performing a conformer search using the low-mode sampling method in the Schrodinger MacroModel software package, with energies being modelled using the OPLS2005 force-field^{51,52}. For each amine, the unique conformers from the search were re-optimized using density functional theory (DFT) at the PBE0/6-311G** level of theory with GD3BJ empirical dispersion correction as implemented in the Gaussian09 software package^{53,54}. The TT, TAPT, and TTBT cations were assigned a charge of 3+, while TAPM cation was assigned a charge of +4. Due to the small energy difference between conformers (< 1.5 kJ mol⁻¹ spread), they have the same chance of forming a low-energy crystal structure; hence, each of these conformers was used as a starting point for crystal structure prediction (CSP) calculations.

CSP was performed using the Global Lattice Energy Explorer (GLEE) program⁵⁵. GLEE uses a low-discrepancy, quasi-random sampling of crystal packing variables to produce a uniform sampling of the lattice energy surface. The ionic structure was kept rigid throughout the initial CSP process. Trial crystal structures were generated across eleven space groups and their lattice energies were minimized until a target number of valid crystal structures was met (Supplementary Table 8). Crystal structures were generated with one cation in the asymmetric unit cell and X anions, where X = 3 for **TT**, **TAPT** and **TTBT**, and X = 4 for **TAPM**. Rigid-molecule lattice energy optimizations were performed using the DMACRYS software⁵⁶. Lattice energies were calculated using an anisotropic atom–atom energy model based on a revised version of the Williams 99 force-field, combined with atom-centred multipoles calculated from a distributed multipole analysis (DMA) of the PBE0/6-311G** density^{57,58}. Multipoles up to hexadecapole on each atom were included, and the polarizable continuum model was applied to DMA to further improve the electrostatic model using a dielectric constant of 3.0. Chloride parameters were taken from the fitting of Hejczyk⁵⁹, while bromide parameters were taken from molecular dynamics studies of ionic liquids⁶⁰. The bromide parameters were deemed suitable from the results of a small CSP test on bromide salts in the CSD (Supplementary Fig. 28,29). Duplicate crystal structures were removed from the final CSP landscape by calculating the similarities of simulated powder X-ray diffraction patterns.

To test sensitivity of CSP to the final energy model and the rigid-cation approximation during lattice energy minimization, predicted crystal structures of **TAPM.Cl** were re-optimized using third order density functional tight-binding theory with self-consistent charges (SCC) as implemented in the

dftb+^{61,62}. The 3OB Slater–Koster parameter files were employed for all simulations and hydrogen-containing pair-potentials were additionally damped using an exponent of 4.0. We corrected for missing London dispersion interactions with the atom-pairwise D3 scheme in the rational damping variant⁵². The SCC tolerance was set to 10^{-5} au and each optimisation was considered converged when the maximum force on each atom dropped below 0.03 eV/Å. The k-point grid sampling was set to achieve a k-point density of at least 0.05 Å⁻¹. Dispersion interactions were accounted for using the D3 correction with the following parameter: $S_6 = 1.0$, $S_8 = 0.0$, $a_1 = 0.841$, $a_2 = 3.834$, within a cut-off radius of 64 Å. These parameters have been previously shown to improve geometrical properties of large molecular crystals upon optimisation⁵⁷. Crystal structures that were deemed a match with experimental crystal structures were further optimised using periodic density functional theory, as implemented in the VASP software package⁶³⁻⁶⁷. The re-optimisation was performed in two steps with the first step involving optimisation of both atomic positions and unit-cell parameters, and the second step involving a single-point energy calculation. All optimisations were performed using the PBE exchange correlation functional with Grimmes D3(BJ) dispersion correction⁵⁴. The projector augmented wave method was used for all calculations with the standard supplied pseudopotentials. A plane wave cut-off of 500 eV was employed in all calculations and k-point sampling was performed using a regular k-point mesh with a k-point density of at least 0.05 Å⁻¹. Optimizations were considered converged when the forces on all atoms were smaller than 0.03 eV/Å.

Synthesis of porous salts

The organic amine linkers were synthesized using previous methods⁶⁸. The halide salts were synthesised by simple dropwise addition of HCl or HBr solutions to the amine linkers and can be prepared on multigram scales. Specific conditions for each salt are provided in the Supplementary Information (Section 2). As an example, bulk powders of **TAPT.Cl** were formed by dissolving **TAPT** (2 g) in a good solvent (*e.g.*, tetrahydrofuran, see Supplementary Table 2 for list of good and bad solvents) at a concentration of 5 mg mL⁻¹. Methanolic HCl was then added dropwise over 5 min with stirring at room temperature. The mixture was stirred for a further 1 h before the solvent was removed under reduced pressure and the resulting solid was washed with tetrahydrofuran, providing crystalline **TAPT.Cl** as an off white solid (2.57 g, 98% yield).

Single crystal growth

Specific crystallisation conditions are given in the Supplementary Information. As an example, single crystals of **TAPT.Cl** suitable for x-ray diffraction were grown by dissolving **TAPT.Cl** (3 mg) in a mixture of methanol (0.5 mL) and chlorobenzene (0.05 mL). The solvent was then left to evaporate at room temperature for 16 h giving block crystals of **TAPT.Cl**.

Crystallography

Powder X-ray diffraction data were collected in transmission mode on powder samples held on thin Mylar films in aluminium well plates using a Panalytical Empyrean diffractometer equipped with a high throughput screening XYZ stage, X-ray focusing mirror, and a PIXcel detector using Cu-K α ($\lambda = 1.541 \text{ \AA}$) radiation. PXRD data for further structural analysis of **TTBT.Cl** were collected on a sample contained in a 0.7 mm borosilicate glass capillary on the same instrument in Debye-Scherrer geometry with a capillary spinner. Data were collected over the range $2^\circ \leq 2\theta \leq 50^\circ$ with a step size of 0.013° over 4 hours and the data were analysed using TOPAS Academic⁶⁹ for indexing, structure solution and refinement. Single crystal X-ray data was measured on a Rigaku MicroMax-007 HF rotating anode diffractometer (Mo-K α radiation, $\lambda = 0.71073 \text{ \AA}$, Kappa 4-circle goniometer, Rigaku Saturn724+ detector); or at beamline I19, Diamond Light Source, Didcot, UK using silicon double crystal monochromated synchrotron radiation ($\lambda = 0.6889 \text{ \AA}$, Pilatus 2M detector). Data reduction was performed using CrysAlisPro. Structures were solved with SHELXT⁷⁰ and refined by full-matrix least-squares on $|F|^2$ by SHELXL,⁷¹ interfaced through the programme OLEX2.⁷² All non-H atoms were refined anisotropically, and all H-atoms were fixed in geometrically estimated positions and refined using the riding model. For full refinement details, see Supplementary Tables 3,4.

HR-TEM

The salt samples were dispersed in chloroform at a concentration of 1 mg mL^{-1} using sonication. The samples were then dropcast onto copper grids. TEM images were obtained using a JEOL 2100+ microscope operating at 200KV and equipped with a Gatan Rio Camera.

Gas sorption analysis

Nitrogen isotherms were collected at 77 K using a Micromeritics ASAP2420 volumetric adsorption analyser. Carbon dioxide isotherms were collected up to a pressure of 1200 mbar on a Micromeritics ASAP2020 volumetric adsorption analyser at 273 K or 298 K. Carbon dioxide isotherms at 195 K were collected using Micromeritics 3flex volumetric adsorption analyser. All samples were activated at 110 °C for 14 h under vacuum for all gas sorptions except for the carbon dioxide isotherms measured at 195 K, where the samples were activated at 353 K for 14 h under vacuum.

Iodine capture experiments

Iodine adsorption tests were performed on five separate samples of each porous salt at 70 °C to volatilize the iodine; the adsorption results were averaged across the five samples. The salt samples were heated under vacuum at 343 K for 16 hours to remove the organic solvent before the iodine capture experiments were performed. To perform the tests the salts were placed into 4 mL vials which were then placed into larger 14 mL vials containing an excess of iodine. The outer vial was then sealed and placed into an incubator at 343 K. At certain time intervals the samples were removed from the incubator and once

cooled to room temperature the inner vial containing the salts were removed and the weight of the vial was measured to monitor the iodine uptake. For each salt, a total of five samples was tested (5 mg of salt). All five samples gave consistent uptakes and the average uptake values were used. To test the recyclability of the salts for iodine capture, the iodine was removed and the capture repeated over five cycles. Due to the high mass of iodine captured in each system and the slow release using vacuum alone, chloroform was first used to remove the bulk of the iodine before the final traces were removed at 70 °C under vacuum for 16 h (Supplementary Fig. 19). Thermogravimetric analysis and PXRD further confirmed the capture of iodine in these three frameworks (Supplementary Figs. S15–S22). To test the recyclability of these salts, the iodine was removed after adsorption by extraction with chloroform, followed by evacuation. Sample colour, thermogravimetric analysis and PXRD data confirmed that the iodine was eventually removed in all three systems. The samples were subjected to five cycles of iodine capture and release, demonstrating excellent recyclability for all three porous salts (Figure 4c, Supplementary Figs. 20,21). PXRD data suggested that a structural change occurs in all three porous salts upon iodine adsorption, as might be expected for such high guest uptakes, but the original guest-free crystal structure was regenerated for all three frameworks after iodine removal (*e.g.*, Figure 4d).

Data availability

Crystal structure data is provided in the Supplementary Information. CSP structures with calculated energies and properties are available at <https://doi.org/10.5258/SOTON/D2857>. The experimentally determined crystal structures, including structure factors, have been deposited as CIFs with the Cambridge Crystallographic Data Centre (entries; 2308598 (TAPM.Cl_P1), 2308599 (TAPM.Cl_P2), 2308596 (TAPM.Br_P1), 2308597 (TAPM.Br_P2), 2308662 (TAPT.Cl)). CIFs are available free of charge at http://www.ccdc.cam.ac.uk/data_request/cif.

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Author contributions. M.O'S. led the experimental work. M.O'S. and R.C. collected gas sorption data. M.O'S. and S.P.A. solved and refined TAPT.Cl crystal structure. M.O'S. carried out all other experimental work including synthesis, crystallisations, SCXRD and PXRD data and iodine uptake experiments and analysis. J.G. and R.H. performed and analysed the CSP calculations. G.M.D. led the computational work. M.B. obtained the HR-TEM data and interpreted it. S.Y.C. carried out powder X-ray diffraction analyses to solve the TTBT.Cl structure. A.C conceived the original idea, supervised the experimental work, and carried out the initial CSP calculations. All authors contributed to the preparation of the manuscript.

Competing interests. The authors declare no competing interests.

Extended Data Fig. 1. Crystal structure prediction suggests dense, non-porous tetrahedral ammonium halide salts. Energy–density landscapes of the CSP structures for **a**, TAPM.Cl and **b**, TAPM.Br coloured by dimensionality of pores within each structure. Black data points (*i.e.*, most structures) are either non-porous or contain isolated cavities. Overlay images for experimental structures (coloured by element) and CSP structures (green) for the two experimentally accessible polymorphs of these two salts; **c**, TAPM.Cl/P1, **d**, TAPM.Cl/P2, **e**, TAPM.Br/P1 and **f**, TAPM.Br/P2. The structural agreement between CSP and experiment is improved by re-optimization of the predicted structures using density functional based tight binding DFTB), which reranks TAPM.Cl/P1 as the second lowest energy predicted structure (Supplementary Fig. 28). The higher energies of the P2 polymorphs can be explained because these experimental structures are solvates (Supplementary Fig. 2), and solvent is not considered here.

Extended Data Fig. 2. A non-metal organic framework by computational design. **a**, Structure of TAPT.Cl, as predicted using CSP (red star in Figure 2a). The accessible pore surface is shown in yellow (1.2 Å probe diameter); **b**, Overlay of the experimental single crystal structure (atom colouring by element), obtained for a partial solvate, and the CSP derived structure (green) for TAPT.Cl.

Extended Data Fig. 3. Structural characterisation of TT.Br and TTBT.Cl. **a**, HR-TEM images of TT.Br; the FFT of the TEM data (top right) is shown with the simulated electron diffraction pattern (bottom right) for the best-matched CSP structure (Fig. 3b), aligned in the zone axis [001] (bottom). **c**, HR-TEM images of TTBT.Cl; the FFT of the TEM data (top right) is shown, highlighting the (010), (020) and (030) planes, with the simulated electron diffraction pattern (bottom right) for the best-matched CSP structure (Fig. 3c), aligned in the zone axis [001]. **c**, Observed (red circles), calculated (black line) and difference (blue line) PXRD profiles for structural refinement of a monoclinic model of TTBT.Cl ($R_{wp} = 1.97\%$, $R_p = 1.51\%$, $\chi^2 = 3.70$). Reflection positions are marked below. Full refinement details are given in the Supplementary Information, Section 2. **d**, Comparison of refined experimental structure for TTBT.Cl and global minimum CSP structure, TTBT.Cl/5.

Extended Data Fig. 4. Alternative structures on the CSP landscape for TATP.Cl. **a**, Lattice energy plot, as colour-coded by largest cavity diameter, highlighting six alternative packings across a range of

physical densities on the leading edge of the landscape for **TATP.Cl**, focusing on structures in low energy ‘spikes’. **b**, Space-filling representations of the six selected **TATP.Cl** structures. **c**, Table summarizing structure ID’s, relative energies relative to the global energy minimum predicted structure, and physical densities of the six highlighted structures, and the observed structure.

Extended Data Fig. 5. Alternative structures on the CSP landscape for TT.Br. **a**, Lattice energy plot, as colour-coded by largest cavity diameter, highlighting the observed polymorph (**TT.Br/7**) and seven alternative packings across a range of physical densities on the leading edge of the landscape for **TT.Br**, focusing on structures in low energy ‘spikes’. **b**, Space-filling representations of the 8 selected **TT.Br** structures. **c**, Table summarizing structure ID’s, relative energies relative to the global energy minimum predicted structure, and physical densities of the eight highlighted structures.

Extended Data Fig. 6. Alternative structures on the CSP landscape for TTBT.Cl. **a**, Lattice energy plot, as colour-coded by largest cavity diameter, highlighting the observed polymorph (**TTBT.Cl/5**) and four alternative packings on the leading edge of the landscape for **TTBT.Cl**, focusing on structures in low energy ‘spikes’. **b**, Space-filling representations of the five selected structures. These structures are defined by ionic tubes and rings comprising 6 chlorides (**TTBT.Cl/5**, **TTBT.Cl/4**), 4 chlorides (**TTBT.Cl/4**), 3 chlorides (**TTBT.Cl/3**, **TTBT.Cl/2**) and 2 chlorides (**TTBT.Cl/1**). Equivalent motifs can be found on the structure landscapes for the other two trigonal linkers; for example, **TT.Br/7** (Extended Data Fig. 5) and has 6-chloride rings, **TTBr/6** and **TATP.Cl/4** (Extended Data Fig. 4) both have a mixture of 4- and 6-chloride rings (*c.f.*, **TTBT.Cl/4**). Also, **TATP.Cl/3**, **TT.Br/5** and **TT.Br/4** are all predicted to form 3-chloride rings (Extended Data Fig. 7). **c**, Table summarizing structure ID’s, relative energies, and physical densities of the five highlighted **TTBT.Cl** structures.

Extended Data Fig. 7. Hypothetical isorecticular non-metal organic frameworks found on the CSP landscapes for three different organic salts. These structures were not observed experimentally, despite investigating multiple solvent conditions (Supplementary Information, Section 2), but they all fall within a lattice energy window that suggests that they could in principle be experimentally accessible (< 40 kJ mol⁻¹ above global energy minimum, see Extended Data Figs. 4–6). All three structures are defined by ionic tubular pores comprising 3 chlorides, unlike the larger ionic pore (A) observed in the three experimental structures (Figure 3f), which is formed by 6 chloride anions. The orange pore surface was calculated using a 1.2 Å probe in each case.

Extended Data Fig. 8. Global property analysis using energy-structure-function maps. The plots show analysis of pore channel geometry and pore limiting diameter for the CSP landscapes of the three trigonal ammonium halide salts. **a–c**, CSP landscapes colour coded for pore channel geometry for **a**, **TAPT.Cl**, **b**, **TT.Br** and **c**, **TTBT.Cl**. **d–f**, CSP landscapes colour coded for pore limiting diameter for **a**, **TAPT.Cl**, **b**, **TT.Br** and **c**, **TTBT.Cl**. All channel dimensionality calculations used a probe radius of 1.65Å.

Extended Data Fig. 9. Carbon dioxide isotherms for porous salts at different temperatures. **a**, **TAPT.Cl**, **b**, **TT.Br** and **c**, **TTBT.Cl**. Filled symbols are for adsorption isotherms, open symbols are for desorption isotherms.