

What's in an atom? A comparison of carbon and silicon-centered amidinium...carboxylate frameworks

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Abstract: Despite their apparent similarity, framework materials based on tetraphenylmethane and tetraphenylsilane building blocks often have quite different structures and topologies. Herein, we describe a new silicon tetraamidinium compound and use it to prepare crystalline hydrogen bonded frameworks with carboxylate anions in water. The silicon-containing frameworks are compared with those prepared from the analogous carbon tetraamidinium: when biphenyldicarboxylate or tetrakis(4-carboxyphenyl)methane anions were used similar channel-containing networks are observed for both the silicon and carbon tetraamidinium. When terephthalate or bicarbonate anions were used, different products form. Insights into possible reasons for the different products are provided by a survey of the Cambridge Structural Database and quantum chemical calculations, both of which indicate that, contrary to expectations, tetraphenylsilane derivatives have less geometrical flexibility than tetraphenylmethane derivatives, *i.e.* they are less able to distort away from ideal tetrahedral bond angles.

Introduction

Numerous derivatives of tetraphenylmethane or tetraphenylsilane have been used in supramolecular and materials chemistry. Functionalization of these building blocks in the 4-position of the phenyl rings gives molecules with divergent functionality, which is ideal for framework formation. Unsurprisingly, a range of metal organic frameworks (MOFs)^[1-10] hydrogen bonded materials (HOFs),^[11-20] and covalently bonded porous materials^[21-26] have been prepared from these tectons. Tetraphenylsilane derivatives are typically significantly easier to synthesize^[27] than their tetraphenylmethane analogues and so would appear to be attractive candidates for framework assembly, although it is not necessarily true that the building blocks are interchangeable. That is, changing the central atom from carbon to silicon may give rise to MOFs/HOFs/COFs with entirely different structures and topologies.

For example, solvothermal MOF growth using zinc nitrate and tetrakis(4-carboxyphenyl)methane $\mathbf{C}^{\text{CO}_2^-}$ ^[28] in DMF/EtOH/water gives MOF-36, which contains a $\text{Zn}_2(\text{carboxylate})_4$ building unit and has a PtS topology.^[3] Indeed, this is

the only MOF topology reported from Zn^{2+} and this ligand;^[29] in contrast reaction of tetrakis(4-carboxyphenyl)silane $\mathbf{Si}^{\text{CO}_2^-}$ with Zn^{2+} cations gives MOFs with a range of structures.^[5-6, 8, 10, 30] When the $\mathbf{C}^{\text{CO}_2^-}$ and $\mathbf{Si}^{\text{CO}_2^-}$ ligands are crystallized with Zn^{2+} under the same conditions, isostructural MOFs are not obtained,^[5] but it is possible to prepare a MOF from $\mathbf{Si}^{\text{CO}_2^-}$ and zinc cations that is isostructural to MOF-36, using a different solvent and reaction temperature.^[10] Similarly, when the same ligands are coordinated to Cu^{2+} , only the PtS MOF has been reported for $\mathbf{C}^{\text{CO}_2^-}$,^[7] while this,^[8] and another^[31] topology have been reported for $\mathbf{Si}^{\text{CO}_2^-}$.^[32] Thus, tetraphenylsilane ligands *can* give the same frameworks as tetraphenylmethane analogues but they often do not. It also appears that silicon-based systems may be somewhat less predictable than those containing carbon.

Similar phenomena are observed when considering hydrogen bonded materials: the neutral tetracarboxylic acid forms of tetrakis(carboxyphenyl)methane and tetrakis(carboxyphenyl)silane, *i.e.* $\mathbf{C}^{\text{CO}_2\text{H}}$ and $\mathbf{Si}^{\text{CO}_2\text{H}}$, can both form hydrogen bonded frameworks. Two crystalline forms of $\mathbf{Si}^{\text{CO}_2\text{H}}$ have been reported, one of which is densely packed,^[33] and one of which has an open HOF structure.^[18] Densely packed^[34] and porous^[18] forms of $\mathbf{C}^{\text{CO}_2\text{H}}$ have also been reported,^[35] but none of the structures match those of $\mathbf{Si}^{\text{CO}_2\text{H}}$. Interestingly however, crystallization of the tetraboronic acids \mathbf{C}^{ba} and \mathbf{Si}^{ba} (Figure 1) gave isostructural hydrogen bonded frameworks containing large channels.^[14] To muddy the waters further, when covalent organic frameworks (COFs) were prepared by thermal self-condensation of \mathbf{C}^{ba} and \mathbf{Si}^{ba} , isostructural materials were formed, but when COFs were prepared by condensation of \mathbf{C}^{ba} and \mathbf{Si}^{ba} with a trigonal hexa-alcohol, different forms were obtained!^[21]

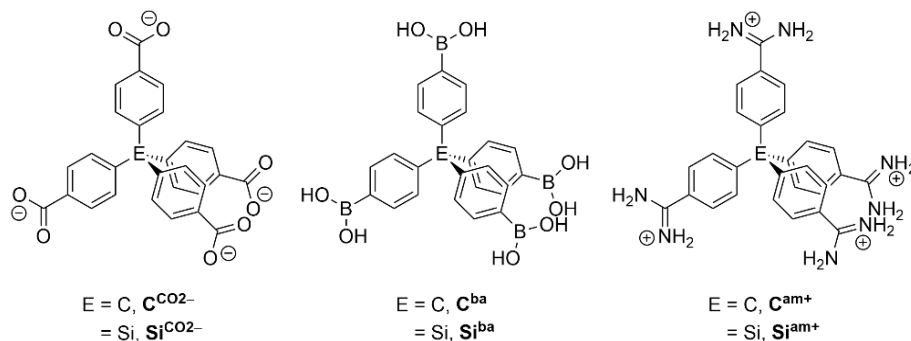


Figure 1. Structure of carbon and silicon-based tectons used to synthesize COFs, HOFs and MOFs.

We have recently reported a general method of preparing hydrogen bonded frameworks from the carbon-centered tetraamidinium $\text{C}^{\text{am+}}$ and polycarboxylate anions.^[16, 20] In this work, we investigate the effect of substituting carbon-based amidinium $\text{C}^{\text{am+}}$ with the silicon-containing analogue $\text{Si}^{\text{am+}}$ when preparing hydrogen bonded frameworks. Specifically, we investigate the assembly of this tecton with terephthalate (TP^{2-}), biphenyldicarboxylate (BPDC^{2-}), C^{CO_2-} and HCO_3^- anions, and combine this with analysis of the Cambridge Structural Database and computational studies to try and understand the effect of this seemingly minor change on product formation.

Results and Discussion

In an attempt to understand the outcomes of changing a central atom from carbon to silicon on framework formation, we first considered the structural implications of this change. Bond lengths at the central tetrahedral atom will increase when moving from a tetraphenylmethane building block to tetraphenylsilane due to the increased lengths of Si–C vs. C–C bonds. Intuitively, one might expect the angles about the central Si atom to be less strictly tetrahedral as these increased bond lengths reduce steric crowding, allowing for greater flexibility. Before attempting to prepare H-bonded frameworks, we decided to examine this assumption by surveying the Cambridge Structural Database (CSD),^[36] and conducting computational studies.

Survey of the Cambridge Structural Database

We searched the CSD^[36] for tetraphenylmethane and tetraphenylsilane fragments using Conquest^[37] (see Supporting Information for search parameters). In the following discussion we include all structures in the CSD containing bond length data and discuss mean values, with standard errors of these means given in parentheses. Selecting only “high quality” structures with $R_1 < 5\%$, or considering median values rather than mean values gives exactly the same trends (see Supporting Information).

As expected, Si–C bond lengths are approximately 0.33 Å longer than C–C bond lengths [1.876(1) vs. 1.548(1) Å] and this increase in length is transmitted to the exterior of the tetraphenyl motif, with the distance from the para-carbon of the phenyl ring (*i.e.* C_4 in Figure 2) to the central atom also approximately 0.33 Å longer [4.682(2) Å vs. 4.354(3) Å]. Surprisingly, angles about the central atom of tetraphenylsilane derivatives are more strictly tetrahedral than in tetraphenylmethane, with $\text{C}_1\text{--Si--C}_1$ angles in tetraphenylsilanes on average 1.87(5)° away from the ideal tetrahedral angle of 109.47°, while $\text{C}_1\text{--C}_{\text{sp}^3}\text{--C}_1$ angles deviate by an average of 3.04(4)°. Again this is transmitted through the building block, with the $\text{C}_4\text{--Si--C}_4$ angles in tetraphenylsilanes closer to ideal in tetraphenylsilanes than the $\text{C}_4\text{--C}_{\text{sp}^3}\text{--C}_4$ angles in tetraphenylmethanes [4.00(9)° vs. 6.06(9)°].

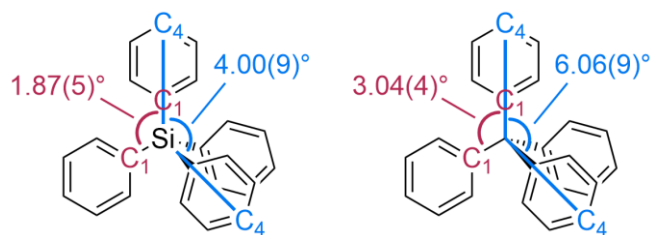


Figure 2. Mean deviation from ideal tetrahedral bond angles for tetraphenylsilane and tetraphenylmethane derivatives in the CSD.^[36] Estimated standard errors of the means are given in parentheses, values in red refer to $\text{C}_1\text{--Si--C}_1$ or $\text{C}_1\text{--C}_{\text{sp}^3}\text{--C}_1$ angles, values in blue refer to $\text{C}_4\text{--Si--C}_4$ or $\text{C}_4\text{--C}_{\text{sp}^3}\text{--C}_4$ angles.

Computational studies

To investigate this further, density functional theory (DFT) studies were conducted using the M06-2X functional and the 6-31G(d) basis set.^[38] Geometry optimization of unsubstituted tetraphenylmethane (CPh_4) and tetraphenylsilane (SiPh_4) revealed that both species have four-fold symmetry (S_4) in the gas phase. In SiPh_4 , four C–Si–C angles are 110.0° and two are 108.4°, *i.e.* the mean deviation from an ideal is 0.7°; in contrast in CPh_4 , four C–C_{sp3}–C angles are 111.7° and two are 105.1°, *i.e.* a mean deviation from ideal of 3.0° (Figure 3).

There may be more steric strain at the central atom in CPh_4 than in SiPh_4 due to the shorter bond lengths, but another factor is the polarity of the bonds involving this atom.^[39] The DFT studies indicate that the Si–C bonds are significantly more polar than the C–C bonds, meaning that the C_1 atoms in SiPh_4 have a significant partial charge (NBO charge = –0.54), while there is only a very small partial charge on these atoms in CPh_4 (NBO charge = –0.03). Thus it appears that the electrostatic repulsion between the δ^- carbon atoms in SiPh_4 enforces a much more rigidly tetrahedral geometry than CPh_4 , despite the latter having greater steric strain. Interestingly, calculations on structures that have been computationally distorted further away from ideal bond angles indicate that it requires less energy to distort SiPh_4 than CPh_4 . That is, while SiPh_4 prefers to be closer to tetrahedral than CPh_4 , it can also accommodate very large deviations from tetrahedral geometries more readily, presumably due to the reduced steric crowding around Si (see Supporting Information for full details).

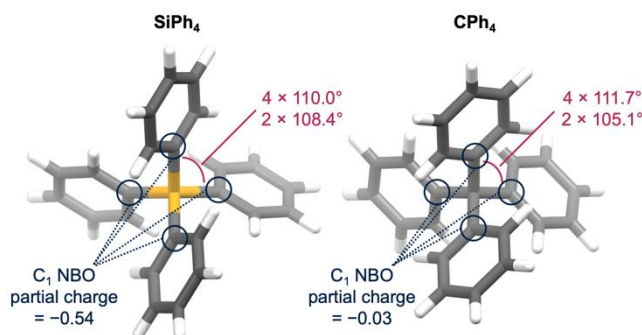
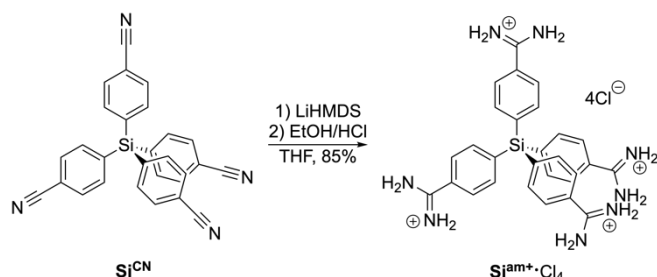


Figure 3. Selected bond angles and NBO partial charges on atoms in fully optimized structures of SiPh_4 and CPh_4 [gas phase DFT calculations, M06-2X/6-31G(d)].

Synthesis and structures of hydrogen bonded frameworks

The new tetraamidinium ligand **Si^{am+}** was prepared in two steps from commercially-available materials. The tetranitrile **Si^{CN}** was prepared from 4-bromobenzonitrile and SiCl₄ as described by Tilley,^[40] and then this was converted to the **Si^{am+}** as its tetrachloride salt in 85% yield using LiHMDS in THF followed by work-up with ethanolic HCl (Scheme 1). Full details are provided in the Supporting Information.



Scheme 1. Synthesis of new silicon tetraamidinium **Si^{am+}.Cl₄**.

Si^{am+} was crystallized with **TP²⁻**, **BPDC²⁻**, **C^{CO2-}** and **HCO₃⁻** anions. In each case, the materials were prepared “in bulk” in reasonable to good yields (38–92%) and fully characterized by SCXRD and PXRD studies, as well as elemental analyses, thermogravimetric analyses and ¹H NMR spectroscopy of the acid-digested frameworks (see Supporting Information). The structures are discussed individually in the following sections, followed by a more general discussion.

Terephthalate frameworks

The crystallization of frameworks from **Si^{am+}** and terephthalate anions appears to be highly dependent on a range of factors including the counteraction of the terephthalate salt, concentration and solvent. These are discussed in turn in the following section.

Cation dependence

We initially mixed solutions of **Si^{am+}.Cl₄** and TBA₂·**TP** in water. This gave mainly fine needle-like crystals that were too small for SCXRD studies, but a few larger crystals that appeared to contain two molecules of **Si^{am+}**, one TBA⁺ cation and five **TP²⁻** anions, with one of these presumably monoprotonated to balance the charge (see SI). NMR studies of the isolated material gave no evidence of TBA cations, suggesting this is a very minor by-product. Nevertheless to avoid these issues, further studies were conducted using the sodium salt of terephthalate, Na₂·**TP**. No evidence of sodium cation incorporation into any of the products was observed.

Concentration dependence

The nature of products obtained from the crystallization of **Si^{am+}** with **TP²⁻** shows a marked concentration dependence. If aqueous solutions of **Si^{am+}.Cl₄** and Na₂·**TP** were mixed to give a mixture with a concentration of **Si^{am+}** of 5.0 mM, immediate precipitation of a fine white powder was observed. NMR and PXRD studies are consistent with this powder being [**Si^{am+}.(TP)₂**] (see later). Repeating the same experiment but with a concentration of **Si^{am+}** of 2.5 mM initially gave a clear colourless solution, which precipitated fluffy clusters of very thin crystals within 10–15 minutes. Despite numerous attempts, we were unable to grow these crystals large enough for SCXRD studies, even when using synchrotron radiation. When the reaction was conducted at a

concentration of 1.3 mM, crystallization took approximately one day to begin. Inspection of the crystals under a microscope indicated that there were some thin needle crystals present, as well as large blocks suitable for SCXRD studies (see later). Conducting crystallization at an even lower concentration (0.50 mM) slowed crystal growth further, with no crystals visible until three days after mixing. The only crystals formed at this concentration were the large blocks.

SCXRD studies on the block-like crystals formed in either the 1.3 mM or 0.50 mM condition indicated that they had the structure shown in Figure 4. The asymmetric unit contains half of a tetraamidinium cation and one terephthalate anion, as well as 7.5 water molecules. One end of the terephthalate anion H-bonds to an amidinium group in a “paired” *R*₂²(8) motif, while the other takes part in a ternary H-bonding motif involving the amidinium cation and a water molecule (Figure 4b). While hydrogen bonding arrangements other than the desired *R*₂²(8) motifs are observed, the overall structure is still of a channel-containing framework. These rectangular channels are approximately 12 × 6 Å in diameter, and are filled with well-ordered water molecules.

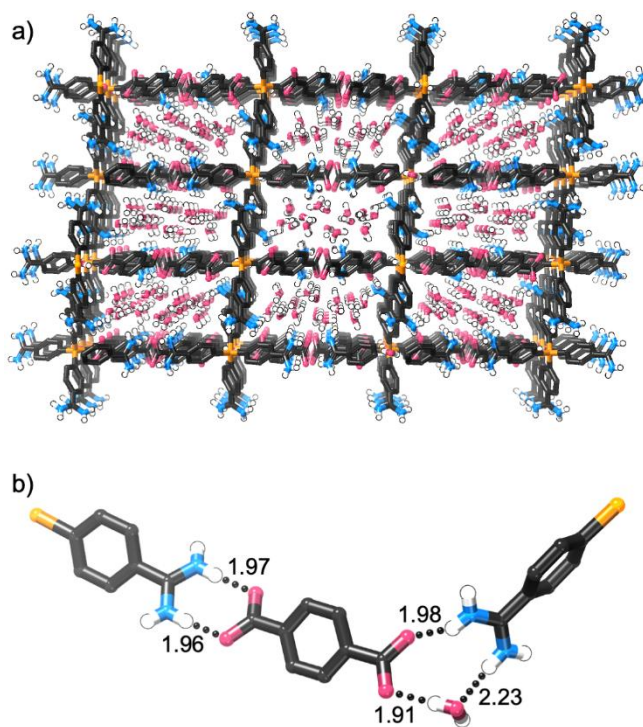


Figure 4. Crystal structure of [**Si^{am+}.(TP)₂**] from water: a) view of packing showing rectangular channels with well-ordered water molecules; b) view of hydrogen bonding arrangements present in the structure showing *R*₂²(8) and “ternary” hydrogen bonding motifs. H···O distances are given in Å, C–H hydrogen atoms are omitted for clarity.

Solvent dependence

While a detailed study of the effect of solvent on product outcome is beyond the scope of this study, we repeated the crystallization of **Si^{am+}** and **TP²⁻** in 1:1 EtOH:H₂O. We have observed in our work on [**C^{am+}.(TP)₂**] frameworks that this solvent mixture slows down crystallization,^[16] which may be due to ethanol’s ability to reduce solvophobic aggregation that occurs in pure water.^[41] Given the importance of concentration on crystallization kinetics and

product outcome, we thought it would be interesting to investigate the effect of solvent on these parameters.

As expected, addition of ethanol slowed down crystallization: at a concentration of 5.0 mM (which caused immediate precipitation when pure water was used), precipitation began after approximately 15 seconds. At a concentration of 2.5 mM, single crystals formed within a few hours. At a concentration of 0.50 mM, no solid precipitated even after 60 days. SCXRD studies were carried out on the crystals grown at 2.5 mM, which revealed that the structure had the expected formula of $[\text{Si}^{\text{am}+}(\text{TP})_2]$. The asymmetric unit of $[\text{Si}^{\text{am}+}(\text{TP})_2]$ from EtOH/H₂O contains one complete molecule of $\text{Si}^{\text{am}+}$, one complete TP^{2-} anion and two half TP^{2-} anions, as well as two EtOH and five H₂O solvent molecules. The two half TP^{2-} anions interact with amidinium groups through "paired" $R_2^2(8)$ hydrogen bonds, and the symmetry of the crystal links the structure into a 1D H-bonded chain (Figure 5). One end of the other TP^{2-} anion H-bonds with an ethanol solvent molecule and this limits the dimensionality of the resulting crystal to one dimension.

PXRD studies

All $[\text{Si}^{\text{am}+}(\text{TP})_2]$ frameworks lose crystallinity upon drying. However, the frameworks' order can be restored by addition of water and this results in relatively complex behavior, with several different crystalline phases and interconversions observed. A brief summary is given here, with a detailed description of all the PXRD studies provided in the Supporting Information.

For each of the frameworks crystallized from water (at four different concentrations), adding a few drops of water to the dried non-crystalline solids resulted in well-resolved PXRD traces within minutes. Interestingly the samples prepared from water at 0.50 or 1.3 mM both transform to a new phase, which does not match either of the single crystal structures. Once formed (within a few minutes), this phase loses a little crystallinity within the first hour, but then stays stable over several weeks. Adding more water, restores the crystallinity to its previous level (Figure 6 and Figure S21).

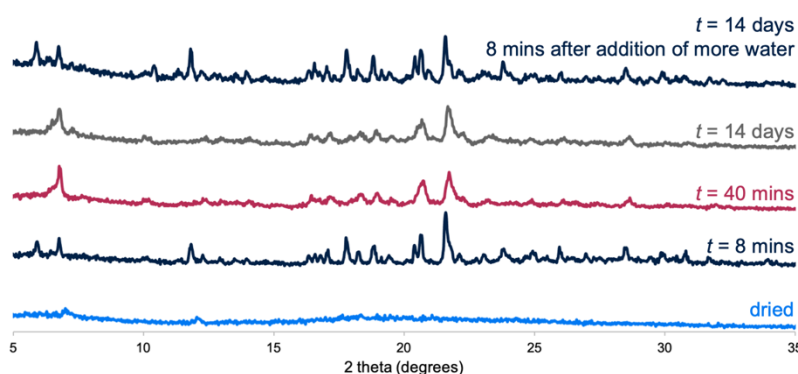


Figure 6. PXRD traces of air-dried $[\text{Si}^{\text{am}+}(\text{TP})_2]$ prepared at 0.50 mM, and the same compound after addition of a small amount of water at $t = 0$ mins. The top trace was recorded on a 14-day old sample 8 mins after adding more water.

Conducting an analogous experiment with the sample prepared from water at 2.5 mM results in the formation of a new phase, which is different to the new phase observed for the 0.50 mM and 1.3 mM samples. This phase loses crystallinity after about an hour, but can be "resuscitated" by addition of more water (Figure S23). Interestingly, the sample prepared at 5.0 mM initially (within a few minutes) transforms into the structure observed in the single crystal structure of $[\text{Si}^{\text{am}+}(\text{TP})_2]$ from water, but then transforms again to a new crystalline phase within a few hours (Figures S24 and S25). This phase then appears to be stable, but addition of more water turns it back to the structure observed in the SCXRD structure of $[\text{Si}^{\text{am}+}(\text{TP})_2]$ from water.

$[\text{Si}^{\text{am}+}(\text{TP})_2]$ prepared from EtOH/H₂O also lost most of its crystallinity upon drying. For this compound, adding water to the sample appeared to convert it to the structure observed in the single crystal structure of $[\text{Si}^{\text{am}+}(\text{TP})_2]$ prepared from water (Figures S26 and S27). Adding EtOH to the dried sample converted it to a poorly-crystalline phase, which appears to be another new phase (Figure S28). It is clear that there are many crystalline solids that can be prepared from $\text{Si}^{\text{am}+}$ and TP^{2-} , two that have been identified by SCXRD studies, and another four identified by PXRD studies. Clearly, the barriers to interconversion between these are very small and there is a remarkable degree of diversity that can be realized from these simple building blocks.

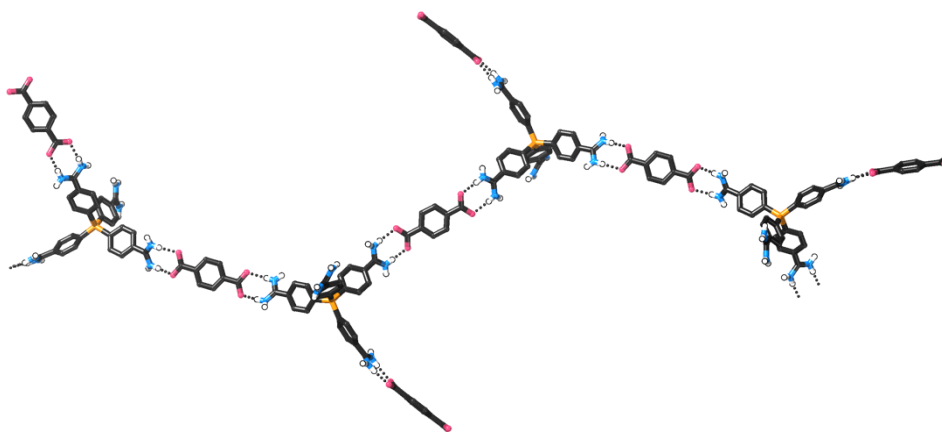


Figure 5. Crystal structure of $[\text{Si}^{\text{am}+}(\text{TP})_2]$ from EtOH/H₂O showing 1D chain structure. C–H hydrogen atoms and solvents are omitted for clarity.

Biphenyldicarboxylate framework

Crystallization of the carbon-centered tetraamidinium $\text{C}^{\text{am+}}$ with biphenyldicarboxylate (BPDC^{2-}) in EtOH/H₂O gives a 15-fold interpenetrated diamondoid framework.^[20] Crystallizing the silicon-centered tetraamidinium $\text{Si}^{\text{am+}}$ with BPDC^{2-} gives a similar highly interpenetrated diamondoid framework (Figure 7), although now with 17 rather than 15 interpenetrated nets (Figure S34). These nets are held together by $R_2^2(8)$ hydrogen bonding arrangements, with H...O distances ranging from 1.87–2.09 Å (69–77% of the sum of the van der Waal radii^[42]). The structure contains relatively small channels (diameter ~ 6.0 Å). These channels appear to contain disordered solvent molecules, although it was not possible to resolve these molecules and so PLATON-SQUEEZE was used to include the electron density in the model.^[43] PLATON-SQUEEZE analysis suggest that this diffuse solvent makes up 31% of the unit cell volume. This is similar to, but larger than, the 25% solvent content in the analogous carbon-based framework $[\text{C}^{\text{am+}}(\text{BPDC})_2]$.

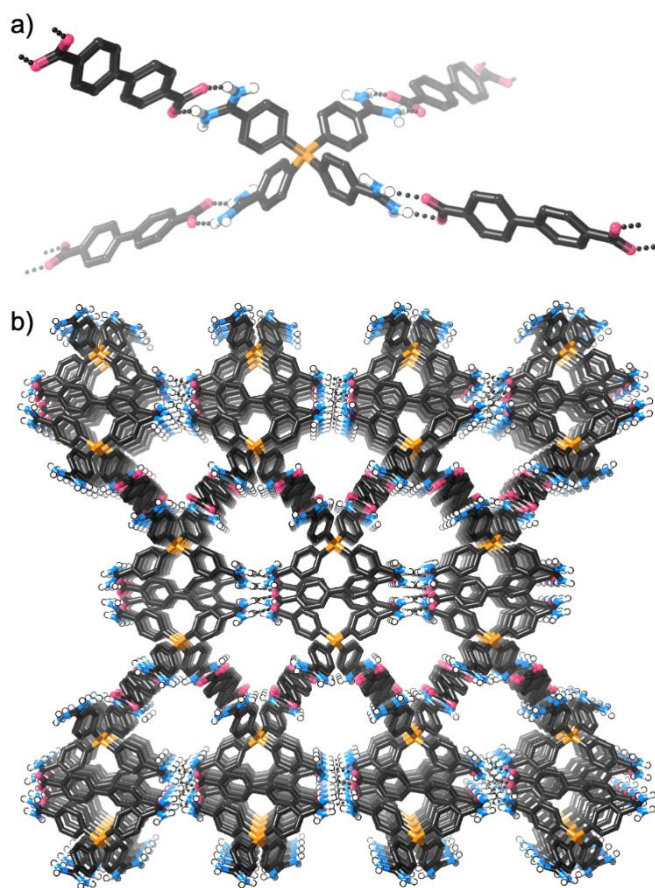


Figure 7. Crystal structure of $[\text{Si}^{\text{am+}}(\text{BPDC})_2]$ a) view of hydrogen bonding arrangement; b) view of packing down the a -axis. C–H hydrogen atoms, and positional disorder of the BPDC^{2-} anion are omitted for clarity. PLATON-SQUEEZE^[43] was used.

Bicarbonate framework

We have previously used the carbon-centered tetraamidinium $\text{C}^{\text{am+}}$ to construct 3D diamondoid frameworks $[\text{C}^{\text{am+}}(\text{HCO}_3)_4]$ assembled through hydrogen bonds to antielectrostatically hydrogen bonded bicarbonate dimers.^[44] We were interested to see whether a similar framework could be assembled using silicon-containing tecton $\text{Si}^{\text{am+}}$, so dissolved $\text{Si}^{\text{am+}}\cdot\text{Cl}_4$ and 50 equivalents of NaHCO_3 in water (an analogous procedure to that used to prepare $[\text{C}^{\text{am+}}(\text{HCO}_3)_4]$). Crystals formed after two days and were analyzed by SCXRD studies. The structure is shown in Figure 8, and is not a diamondoid network as was seen when $\text{C}^{\text{am+}}$ was used. Instead the product has the formula $[\text{Si}^{\text{am+}}\cdot\text{CO}_3\cdot(\text{HCO}_3)_2]\cdot\text{H}_2\text{O}$, with the CO_3^{2-} anion presumably arising from the equilibrium between H_2CO_3 , HCO_3^- and CO_3^{2-} in water.^[45]

Instead of forming a diamondoid network with all amidinium cations hydrogen-bonding to bicarbonate dimers, as was observed in $[\text{C}^{\text{am+}}(\text{HCO}_3)_4]$, the CO_3^{2-} anion in $[\text{Si}^{\text{am+}}\cdot\text{CO}_3\cdot(\text{HCO}_3)_2]$ forms hydrogen bonds to all four crystallographically-independent amidinium groups. Two amidiniums have $R_2^2(8)$ hydrogen bonding arrangements, while two have $R_2^2(6)$ arrangements such that the anion receives a total of six H-bonds with the H...O distance between 1.79 and 2.19 Å (66–81% of the sum of the van der Waal radii^[42]). It is notable that the carbonate anion seems to be at the centre of an ideal hydrogen bonding pocket in the crystal structure, receiving short hydrogen bonds from four cationic donors, and we speculate that this may help bias the equilibrium of the carbonate species towards CO_3^{2-} . The two bicarbonate anions form an AEHB dimer,^[46] and hydrogen bonds to a water solvent molecule link these into a 1D hydrogen bonded chain. The bicarbonate dimer receives a total of six hydrogen bonds from the “sideways-pointing” hydrogen atoms of the tetraamidinium cation. Interestingly, while one of these is moderately short (2.03 Å, 75% of the sum of the van der Waal radii^[42]), the other five are quite long (2.15–2.24 Å, 79–83% of the sum of the van der Waal radii^[42]).

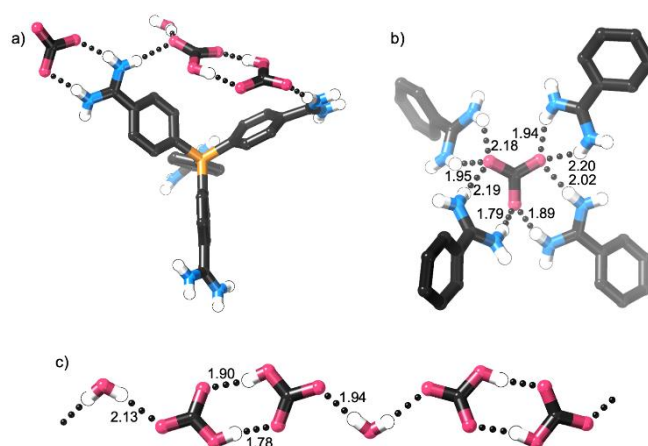


Figure 8. Crystal structure of $[\text{Si}^{\text{am+}}\cdot\text{CO}_3\cdot(\text{HCO}_3)_2]$ a) view of repeating unit; b) view of environment around CO_3^{2-} anion; c) view of antielectrostatically H-bonded dimer chains. H...O distances are given in Å, C–H hydrogen atoms are omitted for clarity.

Tetracarboxylate framework

Dicarboxylate/ HCO_3^- anions seem to give relatively unpredictable frameworks when combined with $\text{Si}^{\text{am}+}$, so we were interested to see what would happen when using the tetracarboxylate C^{CO_2-} . We reasoned that the conformational lock provided by the tetratopic hydrogen bond acceptor may increase the predictability of framework formation, even accounting for silicon's reduced tendency to form the expected networks. Mixing solutions of $\text{Si}^{\text{am}+}$ and C^{CO_2-} in 1:1 ethanol:water gave the six-fold interpenetrated diamondoid framework $[\text{Si}^{\text{am}+} \cdot \text{C}^{\text{CO}_2-}]$ (Figure 9), which is isostructural with the analogous framework prepared from $\text{C}^{\text{am}+}$.^[20,47] The structure contains large square channels, which are filled with well-ordered water molecules in the solid state. The structure is assembled by $R_2^2(8)$ hydrogen bonding motifs, with $\text{H} \cdots \text{O}$ distances of 1.91 and 1.94 Å (71, 72% of the sum of the van der Waal radii^[42]). The framework appears to be robust, and retains its crystallinity upon drying, although we have not yet been able to activate the material to study its gas sorption properties.

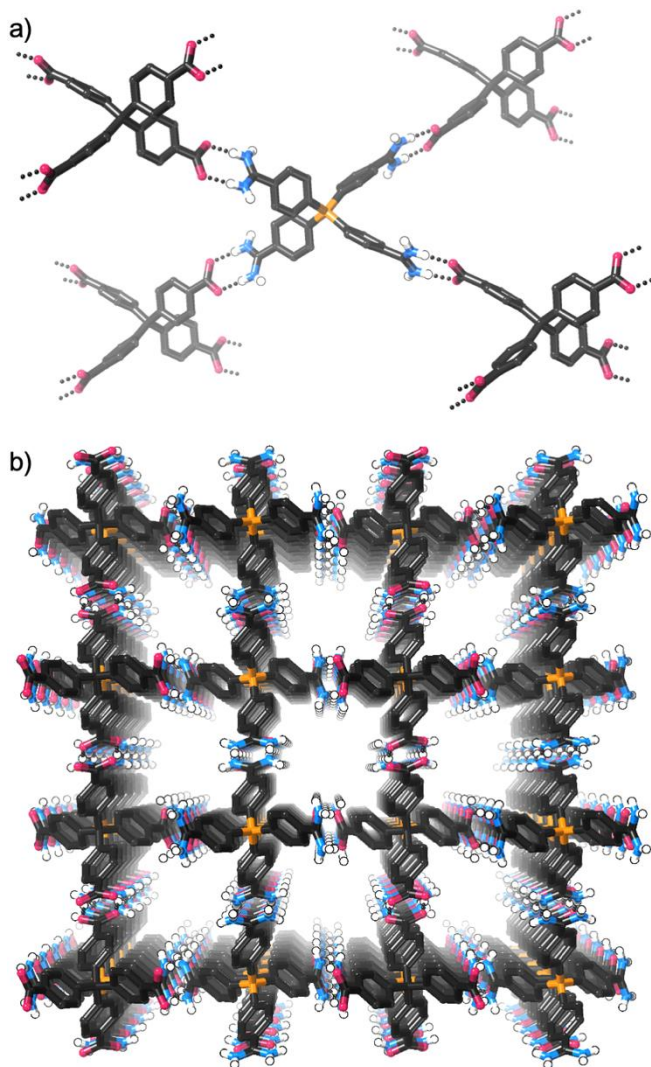


Figure 9. Crystal structure of $[\text{Si}^{\text{am}+} \cdot \text{C}^{\text{CO}_2-}]$: a) view of hydrogen bonding arrangement; b) view of packing down the c -axis. Water solvent molecules and C–H hydrogen atoms are omitted for clarity.

Discussion

The initial starting point of this study was to investigate the similarities and differences between frameworks prepared from silicon-based tetraamidinium $\text{Si}^{\text{am}+}$ and carbon-based tetraamidinium $\text{C}^{\text{am}+}$. It is apparent that none of the silicon frameworks prepared from dicarboxylate/ HCO_3^- anions are isostructural with their carbon analogues, while the silicon and carbon frameworks prepared from the tetracarboxylate C^{CO_2-} are isostructural. While $[\text{Si}^{\text{am}+} \cdot (\text{BPDC})_2]$ forms a *similar* structure to $[\text{C}^{\text{am}+} \cdot (\text{BPDC})_2]$ in that both are highly interpenetrated channel-containing diamondoid networks assembled through $R_2^2(8)$ hydrogen bonding motifs, there are subtle differences. Notably, $[\text{Si}^{\text{am}+} \cdot (\text{BPDC})_2]$ contains 17 interpenetrating H-bonded nets, while $[\text{C}^{\text{am}+} \cdot (\text{BPDC})_2]$ contains only 15. Additionally $[\text{Si}^{\text{am}+} \cdot (\text{BPDC})_2]$ contains a slightly higher solvent percentage (31 vs. 25%), and crystallizes in a tetragonal space group whereas $[\text{C}^{\text{am}+} \cdot (\text{BPDC})_2]$ crystallizes in a hexagonal space group.

While the two crystal structures obtained with terephthalate and $\text{Si}^{\text{am}+}$ are markedly different from the crystal structures previously reported for terephthalate and $\text{C}^{\text{am}+}$, there are some interesting similarities in behaviour. Both $\text{Si}^{\text{am}+}$ and $\text{C}^{\text{am}+}$ give several crystalline phases with TP^{2-} . The carbon-centered amidinium $\text{C}^{\text{am}+}$ gives three different single crystal structures depending on the solvent(s) used in crystallization.^[16] The silicon tetraamidinium gives different structures depending on the solvent used, and also shows an interesting concentration dependence with different singly crystalline phases being obtained from the same solvent (water) when crystallized at different concentrations.

Another similarity between the two sets of terephthalate containing frameworks relates to their crystallinity in response to solvent. The tetragonal form of $[\text{C}^{\text{am}+} \cdot (\text{TP})_2]$ and all forms of $[\text{Si}^{\text{am}+} \cdot (\text{TP})_2]$ lose crystallinity on drying. However, in all cases crystallinity can be recovered by simply adding a drop of solvent, although the phase of the material often differs from that expected based on the SCXRD structure. This behaviour is quite unusual: while it is unremarkable that the three-dimensional lattice collapses when the solvent in the channels is removed, the fact that this 3D ordering can be recovered within a few minutes upon addition of solvent is surprising. On the molecular scale, this must involve the motion and rearrangement of many molecules and hydrogen bonds in a very rapid manner. The large number of structures identified by SCXRD and PXRD suggest that there are many crystalline forms of the framework that differ very little in energy.

Perhaps the starkest difference between silicon and carbon based frameworks occurs for the materials prepared from the tetraamidinium cations and sodium bicarbonate. In this case, the frameworks have essentially no similarity, and indeed the silicon system crystallizes with carbonate and bicarbonate anions, while the carbon-based framework contains only bicarbonate. In both cases, it was necessary to use “forcing” conditions for crystallization, *i.e.* a large excess of anion was necessary and even then crystallization took days to occur. It is perhaps unsurprising that the long crystallization times and large amounts of anion give the system time to find different thermodynamic minima. We note the presence of AEHB interactions in both systems, although again the nature of these interactions differs, with $[\text{C}^{\text{am}+} \cdot (\text{HCO}_3)_4]$ containing dimers that either assemble the framework or are located in the pores of the framework, while $[\text{Si}^{\text{am}+} \cdot \text{CO}_3 \cdot (\text{HCO}_3)_2]$ contains a polymer made up of AEHB dimers linked by water molecules.

It is worth considering why such a large difference is seen between the silicon and carbon based systems. In the silicon-containing systems studied herein, we generally see a smaller deviation from ideal tetrahedral angles at the central atom than in the analogous carbon-containing systems (Table S9), although there are significant variations within the structures of a given cation. It is notable that crystallization of carbon-containing $\mathbf{C}^{\text{am+}}$ with \mathbf{TP}^{2-} , \mathbf{BPDC}^{2-} and HCO_3^- gave open, channel-containing diamondoid frameworks assembled by $R_2^2(8)$ hydrogen bonding arrays for each anion. In contrast, of all the structures prepared from dicarboxylates/ HCO_3^- herein, only $[\mathbf{Si}^{\text{am+}}\cdot(\mathbf{BPDC})_2]$ forms such a network, suggesting that $\mathbf{Si}^{\text{am+}}$ has a reduced tendency to form these predictable frameworks than $\mathbf{C}^{\text{am+}}$. While $\mathbf{Si}^{\text{am+}}$ can deviate from ideal tetrahedral angles, there is an energetic cost to doing so and we suggest this may be a factor in its reluctance to form frameworks. Presumably forming a diamondoid network requires a range of deviations in order to pack effectively, and indeed we note that the silicon atoms in the diamondoid networks $[\mathbf{Si}^{\text{am+}}\cdot(\mathbf{BPDC})_2]$ and $[\mathbf{Si}^{\text{am+}}\cdot\mathbf{C}^{\text{CO}_2-}]$ are significantly more distorted than in all the other structures reported herein (Table S9). We suggest that this distortion provides an extra barrier to framework formation when $\mathbf{Si}^{\text{am+}}$ is used. Presumably, switching from a ditopic to a tetratopic anion means that the energy that can be gained by an optimized hydrogen bonding arrangement outweighs the energetic cost in distorting the central silicon atom.

There are clearly numerous possible products that are very similar in energy in these kinds of hydrogen bonded systems and we suggest that a small barrier such as a more linear central atom may be enough to cause formation of non-diamondoid products. We note that while some flexibility may be advantageous for predictable framework formation, there are clearly limits to this: for example, we were unable to prepare predictable (*i.e.* diamondoid) amidinium...carboxylate frameworks from flexible amino acid-derived dicarboxylates and also found that using larger amidiniums based on tetra(biphenyl)methane scaffolds reduced predictability.^[20] More generally, the vast majority of reported HOFs are derived from relatively rigid building blocks.^[48-50] Given the current interest in the synthesis of hydrogen bonded networks and recent advances in computational prediction of product morphology,^[51-52] we look forward to further advances in our understanding of the role of flexibility in the assembly of these systems.

Conclusion

A survey of the Cambridge Structural Database and Quantum Mechanical calculations reveal that the silicon atom in tetraphenylsilane derivatives tends to adopt a more strictly tetrahedral geometry than the central carbon atom in tetraphenylmethane derivatives. This somewhat counterintuitive result appears to stem from greater electrostatic repulsion between the polar Si–C bonds compared with the non-polar C–C bonds, which constrains the geometries of the SiPh_4 motif to a greater extent, despite the lower steric crowding. A series of hydrogen bonded frameworks were prepared from a silicon-centered tetra-amidinium hydrogen bonding tecton $\mathbf{Si}^{\text{am+}}$ and dicarboxylate anions, and compared with previously-published frameworks based on the analogous carbon-centered tetra-amidinium $\mathbf{C}^{\text{am+}}$. While a series of porous 3D frameworks were prepared from $\mathbf{Si}^{\text{am+}}$, surprisingly the assemblies were much less

predictable despite the preference for a rigidly tetrahedral geometry. This lack of predictability could be overcome by using a tetracarboxylate anion, which did form the expected diamondoid framework. We suggest that some degree of flexibility is helpful in the assembly of hydrogen bonded frameworks to enable favourable packing and the avoidance of unwanted energetic minima during crystallization.

Experimental Section

Details of CSD searches, DFT calculations, and X-ray crystallography are provided as Supporting Information. A brief overview of the synthetic procedures is provided below, with full details and characterization data provided as Supporting Information.

Synthesis of tectons: Tetrakis(4-cyanophenyl)silane \mathbf{Si}^{CN} ,^[40] the dicarboxylate salts $\text{Na}_2\cdot\mathbf{TP}$,^[53] $\text{TBA}_2\cdot\mathbf{TP}$,^[54] and $\text{TBA}_2\cdot\mathbf{BPDC}$,^[20] and the tetracarboxylate salt $\text{TBA}_4\cdot\mathbf{C}^{\text{CO}_2-}$ ^[20] were prepared as previously described. All other compounds were bought from commercial suppliers and used as received. Silicon tetraamidinium $\mathbf{Si}^{\text{am+}}$ was prepared as its tetrachloride salt in 85% yield by treating \mathbf{Si}^{CN} with LiHMDS in THF, followed by work up with ethanolic HCl.

Synthesis of frameworks: Frameworks were prepared by simply mixing a solution of $\text{Na}_2\cdot\mathbf{TP}$, $\text{TBA}\cdot\mathbf{TP}$, $\text{TBA}_2\cdot\mathbf{BPDC}$, $\text{TBA}_4\cdot\mathbf{C}^{\text{CO}_2-}$ or NaHCO_3 in H_2O or 1:1 EtOH: H_2O with a solution of $\mathbf{Si}^{\text{am+}}\cdot\text{Cl}_4$ in H_2O or 1:1 EtOH: H_2O . Depending on solvent and concentration, the time period for crystallization varied from seconds to days. All frameworks were prepared in bulk in reasonable to good yields (38–92%) and were characterized by ^1H NMR spectroscopy of the acid-digested material, IR spectroscopy, elemental analyses, thermogravimetric analysis, SCXRD and PXRD studies.

CCDC 2021298–2021303 contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

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- [1] B. F. Hoskins, R. Robson, *J. Am. Chem. Soc.* **1989**, *111*, 5962–5964.
- [2] B. F. Hoskins, R. Robson, *J. Am. Chem. Soc.* **1990**, *112*, 1546–1554.
- [3] J. Kim, B. Chen, T. M. Reineke, H. Li, M. Eddaoudi, D. B. Moler, M. O’Keeffe, O. M. Yaghi, *J. Am. Chem. Soc.* **2001**, *123*, 8239–8247.
- [4] H. Chun, D. Kim, D. N. Dybtsev, K. Kim, *Angew. Chem., Int. Ed.* **2004**, *43*, 971–974.
- [5] J. B. Lambert, Z. Liu, C. Liu, *Organometallics* **2008**, *27*, 1464–1469.
- [6] R. P. Davies, R. J. Less, P. D. Lickiss, K. Robertson, A. J. P. White, *Inorg. Chem.* **2008**, *47*, 9958–9964.
- [7] L. Ma, A. Jin, Z. Xie, W. Lin, *Angew. Chem., Int. Ed.* **2009**, *48*, 9905–9908.
- [8] R. P. Davies, R. Less, P. D. Lickiss, K. Robertson, A. J. P. White, *Cryst. Growth Des.* **2010**, *10*, 4571–4581.
- [9] C. B. Caputo, V. N. Vukotic, N. M. Sirizzotti, S. J. Loeb, *Chem. Commun.* **2011**, *47*, 8545–8547.
- [10] M. Zhang, Y.-P. Chen, H.-C. Zhou, *CrystEngComm* **2013**, *15*, 9544–9552.
- [11] M. Simard, D. Su, J. D. Wuest, *J. Am. Chem. Soc.* **1991**, *113*, 4696–4698.

- [12] X. Wang, M. Simard, J. D. Wuest, *J. Am. Chem. Soc.* **1994**, *116*, 12119-12120.
- [13] P. Brunet, M. Simard, J. D. Wuest, *J. Am. Chem. Soc.* **1997**, *119*, 2737-2738.
- [14] J.-H. Fournier, T. Maris, J. D. Wuest, W. Guo, E. Galoppini, *J. Am. Chem. Soc.* **2003**, *125*, 1002-1006.
- [15] Y. He, S. Xiang, B. Chen, *J. Am. Chem. Soc.* **2011**, *133*, 14570-14573.
- [16] M. Morshedi, M. Thomas, A. Tarzia, C. J. Doonan, N. G. White, *Chem. Sci.* **2017**, *8*, 3019-3025.
- [17] G. Xing, T. Yan, S. Das, T. Ben, S. Qiu, *Angew. Chem., Int. Ed.* **2018**, *57*, 5345-5349.
- [18] I. Bassanetti, S. Bracco, A. Comotti, M. Negroni, C. Bezuidenhout, S. Canossa, P. P. Mazzeo, L. Marchiò, P. Sozzani, *J. Mater. Chem. A* **2018**, *6*, 14231-14239.
- [19] G. Xing, I. Bassanetti, S. Bracco, M. Negroni, C. Bezuidenhout, T. Ben, P. Sozzani, A. Comotti, *Chem. Sci.* **2019**, *10*, 730-736.
- [20] S. A. Boer, M. Morshedi, A. Tarzia, C. J. Doonan, N. G. White, *Chem. Eur. J.* **2019**, *25*, 10006-10012.
- [21] H. M. El-Kaderi, J. R. Hunt, J. L. Mendoza-Cortés, A. P. Côté, R. E. Taylor, M. O'Keeffe, O. M. Yaghi, *Science* **2007**, *316*, 268-272.
- [22] M. Rose, W. Böhlmann, M. Sabo, S. Kaskel, *Chem. Commun.* **2008**, 2462-2464.
- [23] F. J. Uribe-Romo, J. R. Hunt, H. Furukawa, C. Klöck, M. O'Keeffe, O. M. Yaghi, *J. Am. Chem. Soc.* **2009**, *131*, 4570-4571.
- [24] T. Ben, H. Ren, S. Ma, D. Cao, J. Lan, X. Jing, W. Wang, J. Xu, F. Deng, J. M. Simmons, S. Qiu, G. Zhu, *Angew. Chem., Int. Ed.* **2009**, *48*, 9457-9460.
- [25] W. Lu, D. Yuan, D. Zhao, C. I. Schilling, O. Plietzsch, T. Muller, S. Bräse, J. Guenther, J. Blümel, R. Krishna, Z. Li, H.-C. Zhou, *Chem. Mater.* **2010**, *22*, 5964-5972.
- [26] D. Beaudoin, T. Maris, J. D. Wuest, *Nature Chem.* **2013**, *5*, 830-834.
- [27] For example, all of the silicon-containing building blocks in Figure 1 can be prepared in two steps from commercial materials while the carbon-containing molecules take 4-6 steps. This is because reaction of a lithiated phenyl derivative with SiCl_4 rapidly assembles a functionalised scaffold. The analogous reaction is not possible with CCl_4 and so tetraphenylmethane must either be synthesized or bought (it is relatively expensive), then functionalized.
- [28] Several shorthand names for these molecules have been used in the literature including **TPCM** and **MTB** for the C-centered tetracarboxylate, and **Si4A**, **TPCS** and **STB** for the Si-centered carboxylate. Similarly, the carbon and silicon-centered boronic acids have been referred to as **TBCM** and **TBCS**, respectively. In an attempt to avoid acronym-overload, we have used the abbreviation C^* and Si^* , where $*$ refers to the functionality present: $\text{CO}_2\text{H}/\text{CO}_2^-$ for the tetracarboxylic acid/tetracarboxylate, BO_2H for the tetraboronic acid, and am^+ for the tetraamidinium.
- [29] M. Alnáši, V. Zeleňák, R. Gyepes, A. Zúkal, J. Čejka, *Colloids & Surfaces A*, **2013**, *437*, 101-107.
- [30] Y.-F. Hui, C.-L. Kang, T. Tian, S. Dang, J. Ai, C. Liu, H.-R. Tian, Z.-M. Sun, C.-Y. Gao, *CrystEngComm* **2017**, *19*, 1564-1570.
- [31] T. Guo, X. Yang, R. Li, X. Liu, Y. Gao, Z. Dai, M. Fang, H.-K. Liu, Y. Wu, *J. Solid State Chem.* **2017**, *253*, 129-138.
- [32] A study comparing tetrakis(tetrazolate) ligands based on CPh_4 and SiPh_4 scaffolds seems to show a similar trend: I. Timohkin, J. B. Torres, A. J. P. White, P. D. Lickiss, C. Pettinari, R. P. Davies, *Dalton Trans.* **2013**, *42*, 13806-13808.
- [33] J. B. Lambert, Y. Zhao, C. L. Stern, *J. Phys. Org. Chem.* **1997**, *10*, 229-232.
- [34] N. Malek, T. Maris, M. Simard, J. D. Wuest, *Acta Crystallogr.* **2005**, *E61*, o518-o520.
- [35] Zheng has reported crystalline networks of $\text{C}^{\text{CO}_2\text{H}}$ with nitrogen-containing H-bond donors such as phenazine and 4,4'-bipyridine. We do not include these in this discussion as the H-bonding motif that assembles the network is very different from structures composed of just $\text{C}^{\text{CO}_2\text{H}}$ and $\text{Si}^{\text{CO}_2\text{H}}$. See: Y.-B. Men, J. Sun, Z.-T. Huang, Q.-Y. Zheng, *CrystEngComm*, **2009**, *11*, 978-979; Y.-B. Men, J. Sun, Z.-T. Huang, Q.-Y. Zheng, *CrystEngComm*, **2009**, *11*, 2277-2278.
- [36] C. R. Groom, I. J. Bruno, M. P. Lightfoot, S. C. Ward, *Acta Crystallogr.* **2016**, *B72*, 171-179.
- [37] I. J. Bruno, J. C. Cole, P. R. Edgington, M. Kessler, C. F. Macrae, P. McCabe, J. Pearson, R. Taylor, *Acta Crystallogr.* **2002**, *B58*, 389-397.
- [38] Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.* **2008**, *120*, 215-241.
- [39] An alternative explanation would involve the central carbon atom having to distort to accommodate the steric requirements of the phenyl rings, however NCI analysis (Figure S7) suggests that there is no obvious difference in steric strain between the fully optimised S_4 geometry and structure constrained to have all angles equal to 109.47° .
- [40] F.-Q. Liu, T. D. Tilley, *Inorg. Chem.* **1997**, *36*, 5090-5096.
- [41] M. D. Driver, M. J. Williamson, Joanne L. Cook, C. A. Hunter, *Chem. Sci.* **2020**, *11*, 4456-4466.
- [42] S. Alvarez, *Dalton Trans.* **2013**, *42*, 8617-8636.
- [43] A. L. Spek, *Acta Crystallogr.* **2015**, *C71*, 9-18.
- [44] D. A. Cullen, M. G. Gardiner, N. G. White, *Chem. Commun.* **2019**, *55*, 12020-12023.
- [45] N. J. Williams, C. A. Seipp, F. M. Brethomé, Y.-Z. Ma, A. S. Ivanov, V. S. Bryantsev, M. K. Kidder, H. J. Martin, E. Holguin, K. A. Garrabrant, R. Custelcean, *Chem*, **2019**, *5*, 719-730.
- [46] W. Zhao, A. H. Flood, N. G. White, *Chem. Soc. Rev.* **2020**, DOI: 10.1039/d1030cs00486c.
- [47] SCXRD and PXRD of the dried material are both consistent with a tetragonal structure. If single crystals were mounted directly from the mother liquor they had a different structure, which is still a diamondoid framework but is in a lower symmetry space group. These and other structural transformations of $\text{Si}^{\text{am}^+}\cdot\text{C}^{\text{CO}_2^-}$ and related frameworks will be reported in a future publication.
- [48] Y.-F. Han, Y.-X. Yuan, H.-B. Wang, *Molecules* **2017**, *22*, 266.
- [49] R.-B. Lin, Y. He, P. Li, H. Wang, W. Zhou, B. Chen, *Chem. Soc. Rev.* **2019**, *48*, 1362-1389.
- [50] I. Hisaki, C. Xin, K. Takahashi, T. Nakamura, *Angew. Chem., Int. Ed.* **2019**, *58*, 11160-11170.
- [51] A. Pulido, L. Chen, T. Kaczorowski, D. Holden, M. A. Little, S. Y. Chong, B. J. Slater, D. P. McMahon, B. Bonillo, C. J. Stackhouse, A. Stephenson, C. M. Kane, R. Clowes, T. Hasell, A. I. Cooper, G. M. Day, *Nature* **2017**, *543*, 657-664.
- [52] P. Cui, D. P. McMahon, P. R. Spackman, B. M. Alston, M. A. Little, G. M. Day, A. I. Cooper, *Chem. Sci.* **2019**, *10*, 9988-9997.
- [53] M.-F. Zaltariov, A. Vlad, M. Cazacu, S. Shova, M. Balan, C. Racles, *Tetrahedron* **2014**, *70*, 2661-2668.
- [54] A. J. Lowe, F. M. Pfeffer, *Chem. Commun.* **2008**, 1871-1873.
- [55] N. P. Cowieson, D. Aragao, M. Clift, D. J. Ericsson, C. H. Gee, Stephen J., N. Mudie, S. Panjikar, J. R. Price, A. Riboldi-Tunnicliffe, R. Williamson, T. Caradoc-Davies, *J. Synchrotron Radiat.* **2015**, *22*, 187-190.