



Designing Molecular Building Blocks for the Self- assembly of Complex Porous Networks

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The designed synthesis of complex functional materials such as DNA-functionalized colloidal assemblies or covalent organic frameworks requires understanding how the shape and functionality of the building block impacts synthesizability and final structure. To this end, we use Monte Carlo simulations to demonstrate how vertex-like “molecular” building blocks could self-assemble into ordered, heteroporous networks by introducing chemical specificity to their intermolecular interactions, akin to endowing them with orthogonally-reacting functional sites. The building blocks were modeled as Kern-Frenkel spheres fused together to conform to a vertex-like geometry; and this simple, easily tunable model allowed for the rapid study of the relationship between building block design parameters and their assembled structures. Additional strategies were proposed to avoid ring defects, enhance the extent of crystallinity, and control the relative sizes between the pores of a crystal. The strategies discussed in this paper will aid in the design of molecules that can self-assemble into complex porous structures with potential use for applications ranging from drug-delivery to energy storage and gas separation.

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Designing Molecular Building Blocks for the Self-assembly of Complex Porous Networks[†]

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The creation of molecular or colloidal building blocks which can self-assemble into complex, ordered porous structures has been long sought-after, and so are the guiding principles behind this creation. The pursuit of this goal has led to the creation of novel classes of materials like metal organic frameworks (MOFs) and covalent organic frameworks (COFs). In theory, a tremendous number of structures can be formed by these materials due to the variety of geometries available to their building blocks. However, most realized crystal structures tend to be simple or homoporous and typically assemble from building blocks with high degrees of symmetry. Building blocks with low degrees of symmetry suitable for assembly into the more complex structures tend to assemble into polymorphous or disordered structures instead. In this work, we use Monte Carlo simulations of patchy vertex-like building blocks to show how the addition of chemical specificity *via* orthogonally reacting functional sites can allow vertex-like building blocks with even asymmetric geometries to self-assemble into ordered crystallites of various complex structures. In addition to demonstrating the utility of such a strategy in creating ordered, heteroporous structures, we also demonstrate that it can be used as a means for tuning specific features of the crystal structure, accomplishing such aims as the control of relative pore sizes. We also discuss heuristics for properly designing molecules so that they can assemble into target structures.

1 Introduction

The creation of complex porous networks is critical to many of the problems facing the modern chemical industry such as molecular sieving, gas storage, chemical sensing, catalysis, optoelectronics, fuel cells, and drug delivery¹⁻⁷. Research in this direction led to the creation of several new classes of materials, notably zeolites, metal organic frameworks (MOFs), and covalent organic frameworks (COFs)^{4,7-10}. Researchers are particularly interested in creating complex, porous structures starting from simple molecular building blocks, like organic molecules or shape-anisotropic colloids, and some basic design principles have already been established in this vein¹¹⁻¹³. One such design principle is that a crystal lattice can be decomposed into fundamental, repeating geometric elements, and these molecular building blocks can assemble into this crystal lattice provided that they emulate the crystal's fundamental geometric elements^{10,14-16}. Fundamental

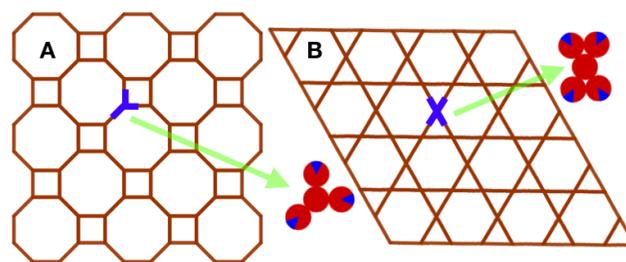


Fig. 1 A schematic of the 4-8-8 tiling or fes net (A) and 3-6-3-6 tiling or kgm net (B) with their vertices are highlighted in blue. The molecular building blocks capable of assembling into these tilings emulate the geometry of their vertices.

geometric elements can consist of polygonal tiles¹⁷, vertex-like molecules^{14,18}, or even secondary building units (SBUs) which have an overall vertex-like geometry but have other features of the crystal, such as smaller pores, pre-built into it^{14,19,20}.

While there exists an immense number of theoretically possible crystal structures, only a small fraction of these have been observed in the laboratory; and these realizable structures tend to be the ones which can be decomposed into building blocks with high degrees of symmetry^{12,21}. This is a reflection of the structures' own high symmetry and relative lack of complexity,

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e.g. homoporosity, which can limit their potential for optoelectronic and conductive applications^{22,23}. Complex or ordered heteroporous structures on the other hand are decomposable into building blocks with relatively low degrees of symmetry, and such building blocks have a tendency to assemble into polymorphous or disordered structures instead of the target structures on which they were based^{15,21}. When a building block has less than perfect geometric symmetry (e.g. an n -topic 2D vertex with less than n -degrees of rotational symmetry), the number of permutations of unique bonding pairs increases, and only a combination of few of these can result in the desired ordered crystal structure. Other combinations can result in the formation of different crystals or no crystals at all. Thus in the absence of control over which combinations of bonds are active in a simulation, polymorphism is likely.

Intuitively, the number of bonding pair permutations can be reduced by selectively tuning whether or not certain functional groups interact, i.e. by making them chemically specific, to the point of forcing the building blocks to assemble into the one target structure. This also serves to make assembly more predictable, providing a stable starting point for tuning features of the crystal, if that should become desirable. This approach has been hypothesized by Zhang²⁴; and in experiment, chemically specific vertex-like building blocks, referred to as "DNA tiles", were able to assemble into the 4-8-8 (fest net) and 3-6-3-6 (kgm net) Archimedean tilings²⁵. In simulation, Whitelam was able to assemble the eight Archimedean tilings from chemically specific, spherical, patchy colloids²⁶. Furthermore, introducing chemical specificity to organic molecules by endowing it with functional groups that react via orthogonal reactions is theoretically feasible, albeit experimentally challenging, with few reported examples²⁷⁻²⁹.

In this work, we use Monte Carlo (MC) simulations to study the self-assembly of complex, porous networks on a two-dimensional surface using vertex-like building blocks, like those shown in Fig. 1. These building blocks consist of hard spheres with attractive patches which stand as proxies for the reactive ends of COF molecules. Capturing the directionality of covalent linkages can be achieved by making these patches narrow. And while these vertex-like building blocks were originally developed as coarse-grained models of COF building units or monomers, they can also be thought of as fused spherical colloids, the synthesis of which is theoretically and experimentally plausible and could potentially be used as building blocks for a wide variety of functional materials for applications like drug delivery³⁰⁻³⁸. By combining this coarse-grained model with MC simulations, we were able to study comprehensively the effect of building block geometry on the final assembled structure. We show that building block geometry is a necessary but insufficient condition for self-assembly into target structures, and that this issue is particularly acute for vertex-like building blocks with lower degrees of symmetry because of their tendency to self-assemble into polymorphous structures. We also show that this polymorphism can be reduced by making the building blocks chemically specific. Additionally, we explore how control of relative pore sizes can be achieved, and how the extent of crystallinity of the structures can be improved. We also discuss

how additional building block design parameters, such as patch angles, could be leveraged to minimize the number of orthogonally reacting functional groups in chemically specific building blocks.

2 Model and Simulation

The molecular building blocks were modeled as hard spheres of diameter $\sigma = 1$ fused together to conform to the geometry of some given vertex. The outermost spheres of the vertex were functionalized with patches of maximum attractive strength $-\varepsilon$ and are analogous to Kern-Frenkel³⁹ patchy spheres. In the Kern-Frenkel model, the full expression for the potential function, u_{ij} , between patchy spheres i and j , consists of an attractive square-well term, u_{ij}^{hssw} , and an orientation-dependent term, f_{ij} , which controls the width of the patches,

$$u_{ij}(r_{ij}; \tilde{\Omega}_i, \tilde{\Omega}_j) = u_{ij}^{hssw}(r_{ij}) \cdot f(\tilde{\Omega}_i, \tilde{\Omega}_j), \quad (1)$$

$\tilde{\Omega}_i$ and $\tilde{\Omega}_j$ are the orientations of the patchy spheres i and j , and r_{ij} is the center-to-center distance. The expression for the square well potential is simply,

$$u_{ij}^{hssw}(r) = \begin{cases} \infty, & \text{if } r < \sigma \\ -\varepsilon, & \text{if } \sigma \leq r < \lambda\sigma \\ 0, & \text{if } \lambda\sigma \leq r \end{cases} \quad (2)$$

where σ is the diameter of the hard spheres, and λ is a pre-factor controlling the center-to-center distance cut-off for u_{ij}^{hssw} . In this work $\lambda = 1.5$. This cutoff is short-ranged enough for the spheres to avoid unphysical interactions with other spheres which are not its nearest neighbors. Each patch, α , points in the direction of some vector, \hat{e}_α , and has an opening width of angle 2δ . In this work, we use $\delta = 10^\circ$. The expression for the orientation-dependence between patchy spheres is then,

$$f(r_{ij}; \tilde{\Omega}_i, \tilde{\Omega}_j) = \begin{cases} 1, & \text{if } \begin{cases} \hat{e}_\alpha \cdot \hat{r}_{ij} \leq \cos\delta, & \text{for some patch } \alpha \text{ on } i \\ \text{and} \\ \hat{e}_\beta \cdot \hat{r}_{ji} \leq \cos\delta, & \text{for some patch } \beta \text{ on } j \end{cases} \\ 0, & \text{otherwise} \end{cases} \quad (3)$$

Monte Carlo simulations were used to investigate the self-assembly of the patchy building blocks. Production runs were conducted in the NVT ensemble, and consisted of 400 or 800 patchy molecules. Before running NVT simulations, an appropriate temperature for the system was identified using Temperature Expanded Ensemble (TEE) simulations^{40,41}, consisting of 24 or 48 patchy molecules, and at the same number density as the later production runs. In TEE simulations, temperatures were changed incrementally, allowing aggregates to constantly break and reform, thus preventing kinetic traps from hindering assembly into the target structures (see Figs. S1 and S2). TEE simulations were used to generate the putative melting curves used to estimate the appropriate temperature neighborhoods at which to

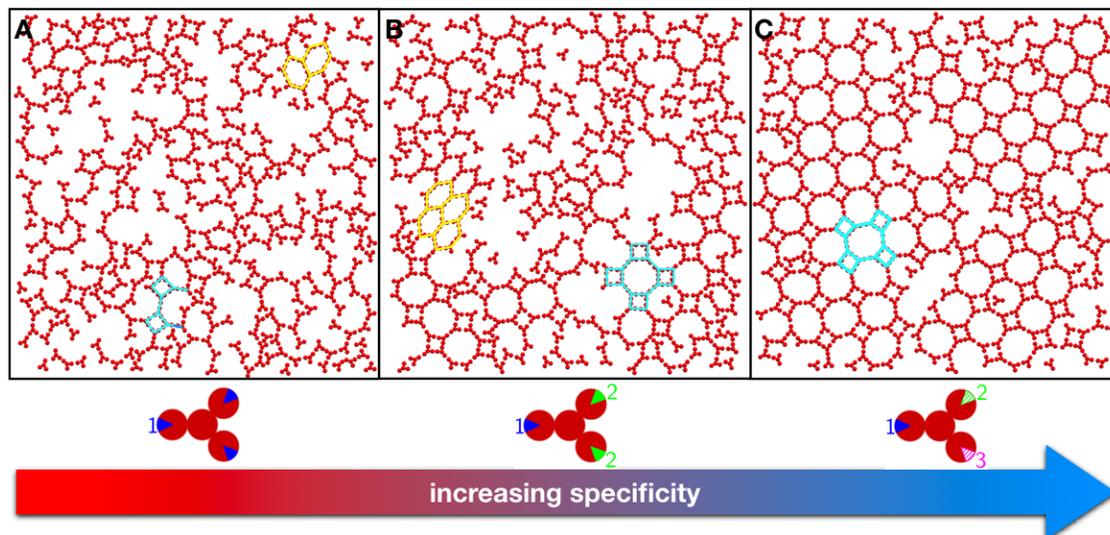


Fig. 2 Making molecular building blocks chemically specific can help prevent polymorphism in assembly. A-C show how increasing chemical specificity affects the quality of crystallites formed by a molecular building block based on the geometry of the 4-8-8 or fes vertex. Select polymorphs are highlighted in yellow and the target fes net is highlighted in cyan. Increasing specificity enhanced porosity and crystallinity and prevented the assembly of polymorphs.

conduct production NVT runs. An example of a putative melting curve can be seen in Fig. S3; and examples of the time evolution of the potential energy for some production NVT runs can be seen in Fig. S4.

Monte Carlo moves for both NVT and TEE simulations not only included single molecule translations and rotations, but also cluster moves. In this work, molecules were considered part of a cluster if the molecules interact. Besides having the typical cluster translations and rotations, the geometric cluster algorithm (GCA)^{42,43} was also employed. The GCA involves randomly selecting a molecule and a pivot point, and then reflecting that molecule about that pivot point. The GCA is a rejection-free algorithm which accelerates and increases the efficiency of sampling configurations⁴⁴. The probabilities of performing a given type of trial move were chosen from prior work which showed they led to an optimal sampling of configurations⁴⁵. In this work, Monte Carlo simulations were performed using the software Free Energy and Advanced Sampling Simulation Toolkit (FEASST).

The building blocks were confined to a two-dimensional surface, and the box length, L_{box} , was chosen such that it accommodated a crystal lattice of high porosity and minimized the entropic packing effects. This ensured that assembly was enthalpically-driven and independent of the initial density, as in experiment. All simulations ran for 48 wallclock hours on a single core each. This typically resulted in TEE simulations having around 10^8 trials, and NVT simulations having $10^7 - 10^8$ trials, depending on the size and number of building blocks involved.

3 Results and Discussion

3.1 Chemical specificity can enhance the ability of building blocks to assemble into complex porous structures

Building block geometries with lower degrees of symmetry (e.g. a tritopic vertex with 2-fold instead of a 3-fold rotational sym-

metry) have a tendency to assemble into polymorphous or disordered networks, even if they were designed to have the right kind of geometry to assemble into some tiling²¹. Less symmetric building blocks have more opportunities to form misbonds, while perfectly symmetric building blocks can only form one type of bond. Thus, if a perfectly symmetric building block has the right shape for some tiling, it can only assemble into that tiling. And while the use of perfectly symmetric building blocks can allow one to obtain crystallites of high quality, the variety and complexity of crystallite structures into which these can assemble are limited. If the goal is to create ordered heteroporous crystallites, then a means to force less symmetric building blocks to assemble into their target structures must be found. Templating could be one such means⁴⁶, but in this work, we are interested in building blocks which can self-assemble into interesting structures without the need for templates or external driving forces. Given this constraint, a plausible strategy is to endow the building blocks with multiple orthogonally-reacting functional groups such that the only bonds possible are the bonds which can propagate into the target structure, i.e., the building blocks can be forced to code for only one structure by making them chemically specific²⁶.

Fig. 2A shows the effect of chemical specificity on a vertex-like building block intended to assemble into the 4-8-8 tiling fes net previously shown in Fig. 1A. This building block has only one type of functional group or patch type, and is not chemically specific. Based on purely geometric arguments, it should assemble into the target fes net, and is indeed capable of doing so (partial assembly of fes net is highlighted in cyan). However, it also partially assembled into unwanted polymorphs (highlighted in yellow), and also resulted in a multitude of misbonds which prevented the system from assembling into large, ordered crystallites of any type. This shows that the correct geometry is a necessary but insufficient attribute for building blocks to assemble into large crystallites of the intended structure.

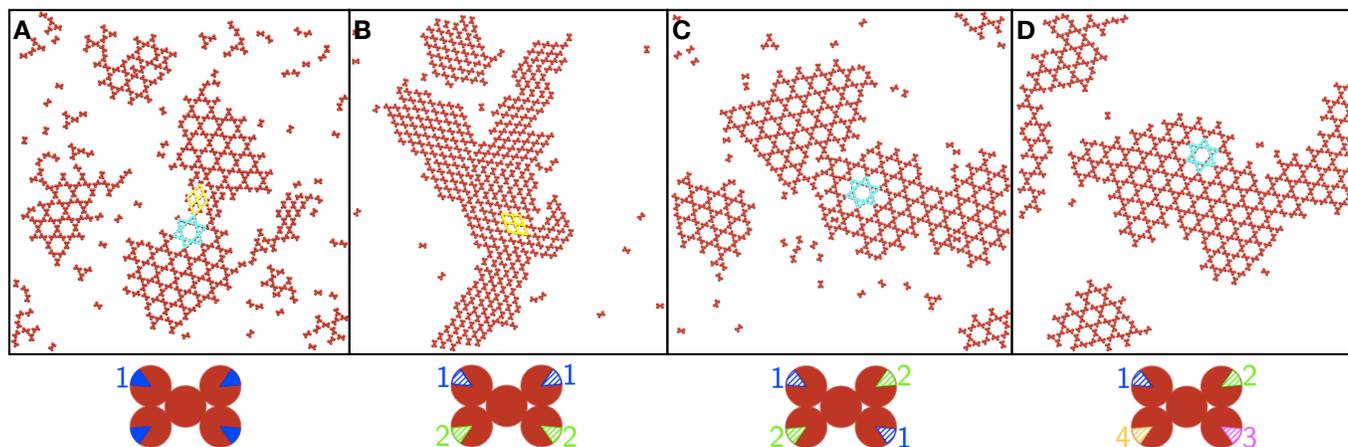


Fig. 3 Chemical specificity needs to be chosen based both on the target structure and the physical constraints on the molecular building block. Shown here are building blocks whose geometry was selected so that they assemble into the kgm net (with different degrees of coloration on the patches). (A) shows a building block with no chemical specificity, and the rhombic (highlighted in yellow) and Kagome lattice (highlighted in cyan) coexist in this system. (B) and (C) show two different specificity schemes for this building block. (B) forms rhombic lattice exclusively, and (C) forms Kagome lattice exclusively. (D) is the building block with an "ideal" number of functional patches, made such that the molecules are incapable of forming strings even for larger patch angles. The interactions in (D) are 1-3, 2-4.

On the other hand, Fig. 2B shows a structure which assembled from a building with the same vertex-like geometry but two kinds of functional groups, as represented by different patch types. In this case, patch types 1 and 2 interact only with the same patch types. This building block was able to assemble into larger crystallites both of the target structure (in cyan) and a polymorph (in yellow). Misbonds can still be observed, but the structure is overall less disordered than the 2A case. In this work, solid colored patches interact only with the same type of patch, while hatched patches interact only with a complementary type of patch. For a complete summary of the interaction schemes used for the chemically specific building blocks in this paper, see TABLE I in the SI.

Finally, the building block shown in Fig. 2C has three kinds of functional groups: patch type 1 which interacts only with other patches of the same type, and patch types 2 and 3 which interact only with each other. This building block was able to self-assemble into fairly large crystallites consisting exclusively of the target fcs net. However, defects are still present: some pores have entrapped molecules, grain boundaries exist between different crystallites, some pores have incomplete closures, and the shape of the pores themselves have subtle deviations, *viz.*, the fcs net should consist of only regular 8-gons and regular 4-gons, but the crystallites in Fig. 2C contains many irregular 8-gons and irregular 4-gons. This is due to the flexibility of bonds which was imparted by having relatively large patch angles. Thus while the addition of chemical specificity can enhance the self-assembly of less symmetric building blocks into large crystallites of the target structure, further refinements in building block design or the system condition have to be made in order to allow assembly into defect-free structures.

Fig. 2 shows that increasing chemical specificity facilitates the self-assembly of building blocks into large, ordered porous structures. The same conclusion can be drawn from analyzing the angular distribution functions (ADFs)⁴⁷, as in Fig. S5A,

and the structural similarity with respect to the perfect lattice, as in Fig. S6. However, there are practical limitations to endowing real molecules with a high degree of chemical specificity. For example, synthesizing organic molecules with multiple orthogonally-reacting functional groups while satisfying strict geometric constraints will be challenging. And even in the case where the vertex-like building blocks are DNA-functionalized anisotropic colloids and the orthogonality between different reacting groups could be achieved by the tuning the sequences of the DNA strands^{25,35,48–52}, creating narrow functional sites consistently on a mass scale will still be challenging⁵³. Therefore, it is highly desirable to determine the minimal number of functional sites necessary for the building blocks to assemble into some complex structure.

3.2 The complexity of chemically specific building blocks can be reduced by leveraging other design parameters

In Fig. 3, we explored whether it is possible to design a building block which can self-assemble into the target structure while being less chemically specific than the "ideal" case. We focus on the vertex-like building block meant to assemble into the 3-6-3-6 tiling or kgm net previously shown in Fig 1B. Fig. 3A shows a structure formed by kgm vertex building blocks with no chemical specificity. Figs. 3B-C show structures formed by building blocks with two patch types and different interaction schemes, while Fig. 3D shows a structure formed by a building block with the "ideal", four patch type interaction scheme. The building block in 3D was the only one expected to assemble exclusively into the target kgm net, but that in 3C was also able to exclusively form this tiling. The building block in 3C is capable of forming strings, but this was not observed in simulations. This is due to other physical characteristics of the building blocks, *viz.*, the narrow width of the patches. If the patch angles were wider, building blocks with this interaction scheme would be more likely to form strings.

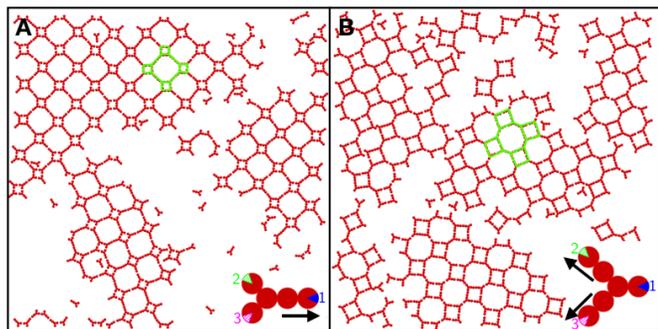


Fig. 4 Simple control of relative sizes between the 4-gons and the 8-gons in a fes net can be achieved by extending some branches of the vertex-like building block without breaking the original rotational symmetry. In (A) the relative size of 8-gons were enlarged, while in (b) the relative size of the 4-gons were enlarged. In both cases, the interaction scheme used for the original building block was preserved because this particular branch extensions did not result in a change in the rotational symmetry. For the interaction scheme used for either of these molecules, see the entry for the fes net or 4-8-8 tiling in Table 1.

However, even for building blocks with narrow patch angles, this does not mean that the scheme used in Fig. 3C is optimal. The structure in the chemically un-specific case in 3A may have shown polymorphous crystallites (the undesired polymorph being the structure formed exclusively in 3B), but the predominant structure by a wide margin is the kgm net. Making adjustments to the simulation or experimental conditions may allow these building blocks to assemble in to the target structure despite having no chemical specificity at all. This implies that in order to design efficient and synthetically feasible building blocks, one must consider the interplay between chemical specificity and other design parameters like the flexibility and directionality of the bonds, the system conditions, and the geometric properties of the target structure.

Making building blocks more chemically specific alone may not necessarily improve its ability to assemble into the target structure, as was shown in Fig. 3. It may also not result in a dramatic enough reduction in polymorphism or disorder to justify the addition of chemical complexity; for example, Fig. 3A still formed relatively large crystallites with predominantly a Kagome structure despite having no chemical specificity. But while the ADF signatures for Fig. 3A is very similar to those for 3C-D, so is the signature for 3B (see Fig. S5B). This implies that ADF signatures cannot be used to quantify whether one has arrived at a design with minimal specificity; and also that more advanced structure characterization methods are necessary to classify different open porous structures^{54,55}.

3.3 Predictability in assembly simplifies the process of tuning features of the crystal for the control of relative pore sizes

In porous network design, strategies for tuning features of the crystal, like controlling pore sizes, is of great interest. For vertex-like molecules, this can be accomplished by extending the branches^{1,9,12,56–60}. Simultaneously extending or contracting all the branches of a building block is similar to scaling a vertex, and

all that this accomplishes is resizing the pores¹⁶. However, a more interesting case is when the branches are of uneven extensions.

In Fig. 4, we explore a case where only some branches of a fes vertex building block were extended, but they were extended in such a way that the rotational symmetry of the original building block was preserved. It can be seen that this kind of manipulation can help achieve control of relative pore sizes. 4A shows a structure with enlarged 8-gons, and 4B shows a structure with enlarged 4-gons. To assemble either structure, it was not necessary to make changes to the interaction scheme used for the original fes building block. But another interesting case to consider is when the selective extension of vertex branches results in reduction of rotational symmetry from the original building block.

Such a case is shown in Fig. 5. Specifically, Fig. 5A shows the structure formed by a three-fold symmetric, tritopic building block, which is known to assemble into the 6-6-6 tiling or hcb net⁹, as was observed in simulation (highlighted in cyan). Because of the high degree of symmetry of this building block, it did not need chemical specificity to self-assemble into the target structure. 5B-D show a desymmetrized version of the hcb vertex building block. The building blocks resulting from this desymmetry now have only a two-fold rotational symmetry. In 5B, it can be seen that when the original chemical specificity, i.e. no specificity, is used for this 2-fold symmetric building block, the building blocks assemble into a disordered porous network of various 6-gons. This implies that altering the rotational symmetry of a building block necessitates a change in the chemical specificity required for the system to assemble into an ordered structure. In 5C, we show the structures formed by a two-fold symmetric building block with two types of patches. This particular system led to the formation of two distinct structures, a homoporous tiling consisting of one kind of irregular 6-gon (highlighted in yellow), and a biporous tiling of two kinds of irregular 6-gons (highlighted in green). In 5D, we show the structure assembled from a two-fold symmetric building block with an interaction scheme which allowed it to assemble exclusively into the biporous tiling previously observed in 5C.

It is promising that precise control over pore sizes and generation of new structures can be achieved by modifying the length of the vertex branches. Tuning features of the crystal by modifying the angles between its vertex branches will be significantly more challenging, particularly for building blocks such as organic molecules, because of the limitations in exactly controlling the geometry of the backbone. Moreover, changing the angles between vertex branches could lead to the formation of radically different minimum energy structures, like false tilings⁶¹ and quasicrystals, and possibly even a reversion into forming the typical periodic lattices^{62,63}.

3.4 Secondary vertex structures as building blocks can enhance the quality of assembled crystallites

The building block used for these nets could be modified in yet another way, by extending one its vertex branches such that the building blocks go from being bisymmetric to asymmetric. This change in rotational symmetry again requires the building blocks

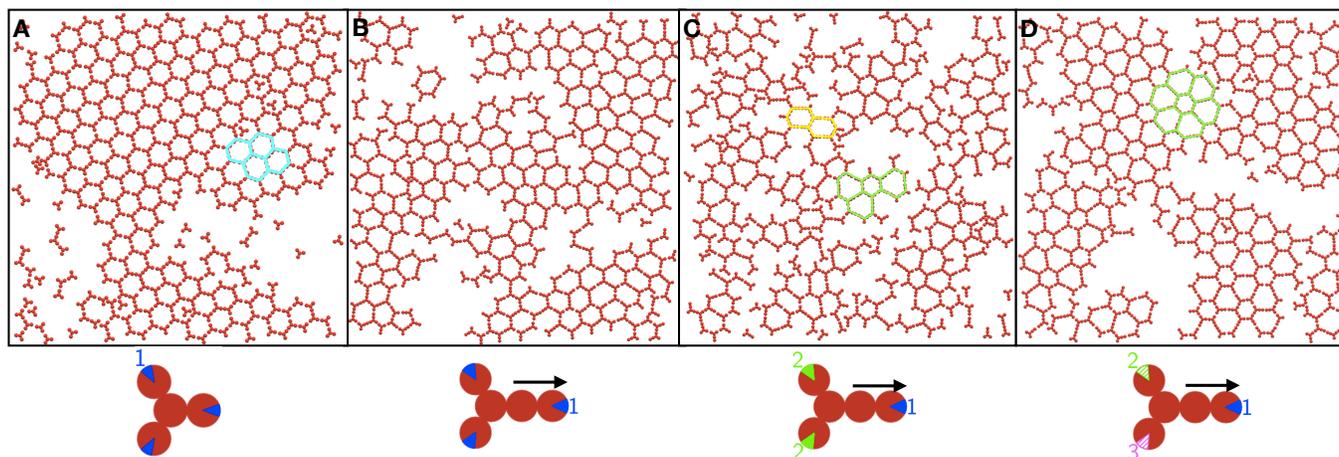


Fig. 5 Modifications in the building block which result in a change in symmetry also requires an update in the interaction scheme to enable the molecules to assemble into ordered, porous structures of the intended geometry. (A) shows a tritopic, 3-fold symmetric molecule intended to assemble into the hcb net or 6-6-6 tiling. This molecule does not require chemical specificity. (B) shows a desymmetrized version of the molecule in (A). This molecule now only has 2-fold symmetry, and preserving the chemical specificity used in (A) rendered this molecule incapable of forming an ordered structure. (C) shows the same desymmetrized 6-6-6 vertex, and the molecules were able to assemble into two clear ordered structures: a homoporous tiling of irregular 6-gons (highlighted in yellow) and a biporous tiling (highlighted in green). In (D), the chemical specificity was updated such that this desymmetrized 6-6-6 vertex will assemble into the biporous tiling highlighted in green.

to have a new interaction scheme, as is shown in Fig. 6. The chemical specificity in this case was chosen so that the building blocks would assemble into a triporous crystal structure, consisting of one irregular 4-gon and two kinds of irregular 8-gons. An alternative interaction scheme would force the system to assemble back into the original fes net, albeit with scaled up pore sizes (see Fig. S7). However, the lack of symmetry of the building blocks also required the use of racemic mixture of chiral vertices, and 6A shows that having multiple components like this hobbled the ability of the system to assemble into large crystallites. The system was clearly capable of assembling into the target structures, and an example of a partially formed target porous network is highlighted in green, but these just did not grow into larger structures. Several factors could have influenced this. The first is the reduced likelihood of complementary patch types finding each other (there are six types of patches in the system in 6A), which could inhibit crystallite growth. A second factor is the formation of intermediate structures that may not be conducive for forming large crystallites of the target structure, particularly if favored intermediates are less rigid than the alternatives.

In Fig. 6B, larger crystallites of the target triporous tiling were assembled when the building blocks emulated the geometry of a secondary vertex structure consisting of the chiral vertices of the system in 6A fused together. The use of the secondary vertex geometry allowed for a single component system and also reduced the number of patch types in the system to four. However, the crystallites shown in 6B are not as large as the ones shown in Fig. 2C and Fig. 4, which all have three patch types. The precise reason why building blocks based on secondary vertex structures improves crystallite quality is still unclear, but this consistently tends to be the case whether using another kind of building block based on an asymmetric vertex, such as the building block for the fxt net or 4-6-12 tiling shown in Fig. S8 or a bisymmetric, tritopic building block meant to assemble into the hca net or 3-12-12 tiling,

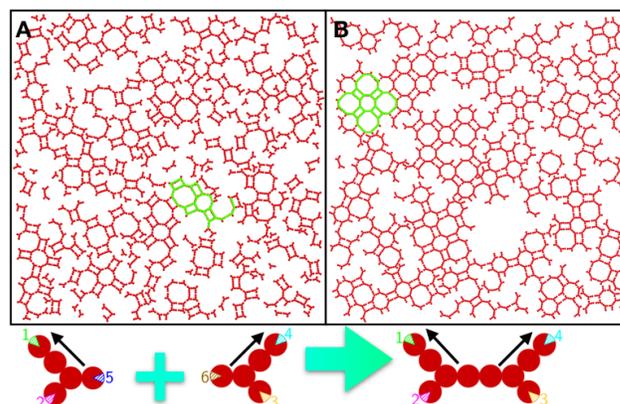


Fig. 6 A tiling with a chiral vertex needs to be assembled from a racemic mixture of chiral vertices (A) or a single-component system where these vertices are fused together (B). The single-component system in (B) allowed for the formation of larger triporous crystallites. The active interactions in these systems are: 1-4, 2-3, and 5-6 if such patch types exist.

as in Fig.S10. In the latter case, using a secondary vertex building block increased the rigidity of the structure and this helped eliminate the formation of deformities like 10-gon pores. Further study needs to be done whether the resulting improvement in the quality of the assembled crystallite is due to increased rigidity provided by using a secondary vertex structure, or the reduction in the number of patch types, or the prevention of assembly into unwanted intermediate structures that hinders overall crystallite growth. Additionally, controlling the relative pore sizes of structures assembled from secondary vertex building blocks follows the same principles which have just been discussed (see Fig. S9).

3.5 Other design considerations

So far it has been shown that the addition of chemical specificity to building blocks is a sound strategy for inhibiting misbonds and polymorphism. Some basic design considerations for the control of relative pore sizes have been considered; and the relation between the geometric symmetry of the building block and chemical specificity was elucidated. A method, *viz.* the use of building blocks based on secondary vertex structures, for further improving the quality of crystallites has also been discussed. These techniques were implemented to assemble the eleven regular and semi-regular tilings, shown in Fig. 7. The assembly of these tilings without polymorphism made it necessary to have the less symmetric building blocks chemically specific. It also became necessary to use secondary vertex structures for the building blocks used in 7E and 7J to prevent ring defects. Furthermore, in Fig. 7F, the narrow patch widths were leveraged to enable the formation of the target kgm net using a reduced number of patch types.

But once again, the absence of polymorphism does not mean that the crystallites are necessarily free of defects. The snapshots in Fig. 7 show grain boundaries, molecules entrapped between pores, incomplete closure of pores, and vacancies within crystallites. The same defects were observed by Whitelam when he reproduced these eleven tilings using chemically specific spherical patchy colloids²⁶. The interaction schemes used by Whitelam to assemble certain tilings differ from some of the interaction schemes used in Fig. 7 because the interaction schemes in this paper were chosen to leverage other design parameters like the directionality of linkages and the rigidity provided by using secondary vertices. A table summarizing the interaction schemes used for the building blocks in Fig 7 can be seen in Table 1.

There still remains many other design parameters that have not been discussed which also affect a system's tendency to polymorphism and disorder. It was previously described how the use of secondary vertex building blocks can enhance the rigidity of the structure, which can then prevent the formation of ring defects. Another design parameter that can help enhance rigidity is the patch angle, which is a proxy for the directionality of interactions and the flexibility of the bonds. Directional interactions is one of the reasons why COFs are capable of forming open porous networks. Having wider patches increases the number of accessible angles between vertex branches; consequently, this increases the tendency towards polymorphism, since the number of polygons capable of being formed also increases.

Nevertheless, large patch angles could be advantageous for the assembly of porous networks in high density systems, where it may become impossible for molecules with strict directionality to close into the accessible polygons. In this case, the final assembled structure may not be apparent based on the geometry of the building block and could even be density-dependent⁶³. For example, certain patch angles could result in periodic false tilings⁶¹, or possibly even quasi-crystals⁶⁴.

Thus, when the lack of structural rigidity is combined with the additional design space provided by different possible interaction schemes, there is little predictability in what structures building blocks can form. For example, this can result in something like a biporous structure consisting of 4-gons and 8-gons assembling from building block based on the vertex for the triporous 4-6-12 tiling or fxt net (see Fig. S8). In this case, an algorithm for hypothetical structure prediction similar to the automated assembly of secondary building units (AASBU) method developed by Caroline Mellot-Draznieks *et. al.*^{65,66} could aid in building block design. Such methods potentially could be very helpful in enumerating structures based purely on geometrical constraints but more work is to incorporate chemical constraints in such methods.

Another issue that should be brought up is the feasibility of the patch angles used in this work. The organic molecules used to assemble COFs are highly directional⁴, but synthesizing an organic molecule with multiple orthogonally reacting functional groups while conforming to precise geometric requirements will be challenging. And in cases where interactions are more easily tunable, like for DNA-functionalized colloids, creating narrow functional patches necessary to maintain the strict directionality required for assembling open porous networks with any consistency will still be difficult⁵³.

A final consideration is how effective the addition of chemical specificity will be for 3-D assembly. In this case, chemical specificity will still eliminate many of the permutations in the different types of bonds and reduce much of the uncertainty in the assembly. However, unlike the 2-D case, using even the highest level of chemical specificity does not guarantee the reduction of possibilities into just one structure. A further complication is that stacking interactions critically influence the ability of planar molecules to assemble into porous COFs^{67,68}. The interplay between this and

Table 1 Attractive pair interactions for the tilings shown in Fig. 7. Attractive pair interactions reference the patch colors of the building blocks used to assemble into the tilings.

Tiling	RCSR Net Code	Snapshot	Attractive Pairs
1-1-1	hxl	7A	1-1
2-2-2	sql	7B	1-1
3-3-3	hcb	5A, 7C	1-1
4-8-8	fes	2C, 7D	1-1, 2-3
3-12-12	hca	7E	1-2
3-6-3-6	kgm	3C, 7F	1-2
3-3-3-3-6	fsz	7G	1-1, 2-3, 4-5
3-3-3-4-4	cem	7H	1-1, 2-5, 3-3, 4-4
3-3-4-3-4	tts	7I	1-1, 2-3, 4-5
4-6-12	fxt	7J	1-2, 3-4
3-4-6-4	htb	7K	1-2, 3-4

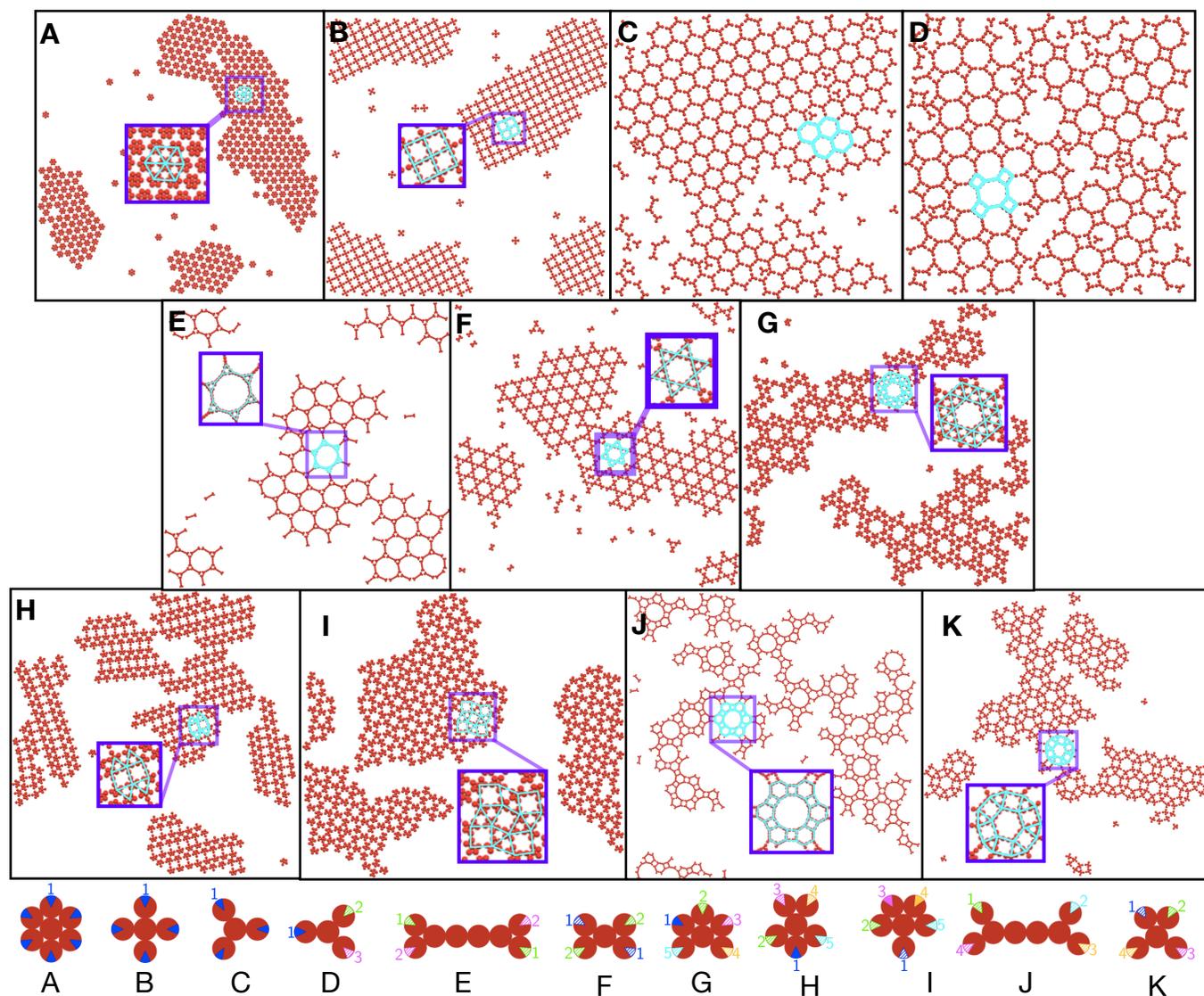


Fig. 7 Self-assembly into the eleven edge-to-edge tilings by regular polygons. A-C are Platonic tilings. These tilings are homoporous and their building blocks do not require chemical specificity to assemble into ordered structures of the target tiling. D-K are the Archimedean tilings, which are heteroporous. The building blocks for these require chemical specificity to assemble into the target structures without also forming polymorphs. Additionally, the building blocks for (E) and (J) consist of two vertex-like building blocks fused together. The interaction schemes used for the Archimedean tilings can be found on Table 1.

inherent polymorphism is an area of further study.

4 Conclusions

In this work we used a "patchy molecule model", consisting of Kern-Frenkel spheres fused together, to study the assembly of vertex-like building blocks with directional interactions. These building blocks can be thought of as organic molecules or DNA-functionalized anisotropic colloids.

We found that the incorporation of chemical specificity to building blocks with lower degrees of symmetry can help eliminate the occurrence of misbonds and polymorphism, and enhance the assembly of ordered heteroporous crystallites. Chemical specificity can force the building blocks to assemble into a specific structure, and this leads to a predictability that can provide a starting point for the modification of features of the crystal lattice itself. The

ability to tune the relative sizes between the pores is an example of this. In this work, it was demonstrated that control of relative pore sizes could be accomplished by extending some of the branches of the building blocks. The interplay between implementing this method and chemical specificity was also studied, and it was found that as long as the extension of branches does not result in a change in the degree of symmetry of the building block, the chemical specificity does not have to be updated from the original. It was also found that the quality of crystallites could be improved further by using building blocks which conform to the geometry of secondary vertex structures. The use of secondary vertex building blocks is effective because it can reduce the number of molecular components in the system, and it can also add further rigidity to the structure which helps prevent the formation of defects. Other design parameters, like the

patch angle (proxy for the directionality of interactions) was also discussed. Of particular interest is that physical characteristics of the building block, like its patch angle, could be leveraged to reduce the number orthogonally reacting patch types needed for the building blocks to assemble into the target structure. All these discussed techniques were then used to design building blocks which self-assembled into the eleven regular and semi-regular tilings without the presence of polymorphs.

The extension of the current patchy model to study the 3-dimensional assembly of planar molecules, such as 2-D COFS, and the assembly of non-planar molecules to form 3-D porous networks will be the subject of future work. In this regard, recent work by Nguyen and Grünwald⁶⁸ on the 3-D assembly of planar COF building blocks can serve as an important reference to test any resulting simple model.

This work showed that chemical specificity in building blocks from the addition of multiple orthogonally-reacting functional groups is a powerful tool for achieving high-level materials design and the creation of non-trivial porous structures. However, other design parameters could still be leveraged either to reduce the need for chemical specificity or to further improve crystallinity.

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We leverage building block geometry and intermolecular interactions to facilitate self-assembly into ordered, heteroporous networks.

