

How to design an icosahedral quasicrystal through directional bonding

Eva G. Noya,^{1, a)} Chak Kui Wong,² Pablo Llombart,¹ and Jonathan P. K. Doye^{2, b)}

¹⁾*Instituto de Química Física Rocasolano, Consejo Superior de Investigaciones Científicas, CSIC, Calle Serrano 119, 28006 Madrid, Spain*

²⁾*Physical and Theoretical Chemistry Laboratory, Department of Chemistry, University of Oxford, South Parks Road, Oxford, OX1 3QZ, United Kingdom*

(Dated: 25 May 2021)

Icosahedral quasicrystals (IQCs) are materials that exhibit long-range order but lack periodicity in any direction in space. Although icosahedral quasicrystal (IQCs) were the first reported quasicrystals (QCs) in Shechtman’s groundbreaking 1984 paper¹, they have only been experimentally observed in metallic alloys² and never for other materials. By contrast, QCs with other symmetries (particularly dodecagonal) have now been found in a growing number of soft-matter systems^{3–5}. Here we introduce a new class of IQCs built from model patchy colloids that could be experimentally realized using DNA origami particles. Our rational design strategy leads to systems that in simulations robustly assemble into a target IQC through directional bonding and is illustrated for both body-centred and primitive IQCs with the simplest systems involving just two particle types. The key design feature is that the geometry of the inter-particle interactions favours the propagation of an icosahedral network of bonds even though this leads to many particles not being fully bonded. As well as furnishing model systems to explore the fundamental physics of IQCs, our approach provides a potential route to functional quasicrystalline materials.

^{a)}Corresponding author: eva.noya@iqfr.csic.es

^{b)}Corresponding author: jonathan.doye@chem.ox.ac.uk

29 A common guiding principle to understand why quasicrystals form is the presence of two
 30 length scales in the interparticle interactions^{6,7} (or equivalently features at two wavenumbers
 31 in the Fourier transform of the potential). For ultrasoft potentials, if the ratio of the two
 32 (inverse) length scales is equal to the golden ratio, then IQCs can be stabilized⁸. Similarly,
 33 for potentials representing particles with hard repulsive cores, one-component systems that
 34 can form IQCs in simulations have been located by scanning the parameter space of model
 35 potentials with multiple minima^{9,10}.

36 But are long-range features in the potential necessary for IQCs or can local directional
 37 bonding that encourages the symmetry of the quasicrystal be sufficient to stabilize IQCs?
 38 For QCs with dodecagonal symmetry the equivalent questions have been resolved by a 2D
 39 two-component mixture of patchy particles¹¹. The local directional bonding favours square-
 40 triangle tilings and quasicrystalline fully-bonded configurations are possible where bonds are
 41 equally likely in any of twelve equivalent directions.

42 Interestingly, in the structural analysis of the IQCs of Refs. 9 and 10, although the
 43 potentials were isotropic, the bonds were clearly directed along the symmetry axes of the
 44 icosahedral point group. However, there is no known interparticle network with icosahedral
 45 symmetry where all particles are fully bonded. For example, it is well known that 12-
 46 coordinate local packing with icosahedral order is frustrated¹². Although it is possible to
 47 have small clusters that are polyicosahedral packings, the rapid build-up of strain energy
 48 due to the increasingly wide distribution of bond lengths makes these packings only feasible
 49 at small sizes¹³. Similarly, despite significant efforts to find a tetrahedrally-coordinated
 50 network that is an IQC, this goal has not been achieved¹⁴.

51 Another interesting feature of the IQCs of Refs. 9 and 10 is that although they have near-
 52 perfect long-range orientational order, they are very heterogeneous at a local level with, for
 53 example, broad distributions of the coordination number. Perhaps, therefore, a way forward
 54 in our quest to design IQCs that are stabilized through directional bonding is to forego the
 55 usual goal of full bonding. Here, we show that, building on this insight, it is surprisingly
 56 straightforward to design systems of patchy particles that robustly assemble into IQCs, and
 57 which could be potentially realized using DNA nanotechnology, as has been the case for the
 58 above mentioned patchy-particle dodecagonal quasicrystal¹⁵.

Design strategy

The strategy used to design patchy model systems that form IQCs builds on our recent work on the assembly of complex periodic crystals¹⁶. In the periodic case, each unique atomic environment in the target structure is replaced by a patchy particle whose patches point directly at its neighbouring particles. The directional bonding is mediated by specific interactions between the patches with the potential also including a torsional component.

As target structures, we use ideal models of IQCs generated by the cut-and-project method¹⁷. Our first example is a QC obtained by projecting a 6D body-centred hypercubic lattice onto the physical space using a dodecahedral occupation domain; such a QC is designated as body-centred icosahedral (BCI). Inspection of the ideal QC structure (Fig. 1a), together with its $3/2$ rational approximant (Fig. 1b), reveals the presence of clusters with icosahedral symmetry with an inner triacontahedron surrounded by a layer of four-coordinate particles (Fig. 1d). The unit cell of the $3/2$ approximant contains two such complete clusters organized in a body-centred-cubic lattice in a matrix of particles that glue together the clusters. By contrast, in the ideal QC, the clusters are often imperfect.

We have identified eleven local environments with coordination number between two and seven in the IQC, that are reduced to seven in the approximant (Fig. 1c). These local environments can be grouped into five classes, with environments in a given class only differing by the absence of one or two bonds. If we were to represent each local environment with a separate particle type, this would lead to a cumbersome 11-component mixture. Instead, we represent each environment class by a single patchy particle with the same number of patches as the most-bonded environment in that class (Fig. 1e). Thus, some fraction of particles will not be fully bonded even in the target structure. The red and green particles are designed to form the triacontahedra, and the blue, yellow and purple particles a network that links together these clusters.

Icosahedral quasicrystal assembly

The ability of this model system to form an IQC was tested by performing simulations of a low-density fluid, choosing the conditions to enable the nucleation and growth of a single solid cluster. Fig. 2a provides an example of a resulting cluster. Despite the rather

irregular shape of the aggregate, if one examines the configuration closely one can see that all the triacontahedra are oriented with a five-fold axis out of the plane. This long-range orientational order is confirmed by the bond-orientational order diagram (BOOD) which displays clear icosahedral symmetry with bonds being oriented along the five-, three- and two-fold axes. The icosahedral quasicrystallinity is confirmed by the diffraction patterns, which are very similar to those for the ideal IQC and exhibit the five-, three- and two-fold symmetries characteristic of the icosahedral point group (Fig. 2b and Extended Data Fig. 2).

To illustrate the generality of our approach, we have considered a second target structure, namely a primitive icosahedral (PI) QC. By projecting the 6D primitive hypercubic lattice onto the 3D physical space with a dodecahedral occupation domain, we obtain an ideal IQC and a $8/5$ rational approximant (Extended Data Fig. 3). In both structures, we identified the icosahedral cluster depicted in Fig. 3a as a key building block. The cluster consists of concentric shells, which, starting from the inner shell, are a dodecahedron, a Mackay icosahedron, a rhombicosidodecahedron, and a icosidodecahedron.

In preliminary simulations with just the three patchy-particle types necessary to form this basic cluster (Fig. 3b; the red particles form the dodecahedral core and the green and blue particles the outer shells), we found that these particles on their own were able to form an IQC without any need to consider the other environments present in the ideal IQC or the approximant. A resulting large assembly, oriented along the five-fold axis of symmetry, is depicted in Fig. 3c. The BOOD again exhibits icosahedral symmetry, but for this system bonds are only oriented along the two- and three-fold symmetry directions. The diffraction patterns confirm the system is an IQC (Fig. 3d); note that the diffraction pattern along the two-fold axis is substantially different from that for the BCI QC in Fig. 2b and has features that are very similar to the ideal PI QC (Extended Data Fig. 5).

Design simplification

We next considered if the two IQC-forming systems could be simplified further, because of the general interest in understanding how much information needs to be programmed into the particle interactions to achieve a given assembly target,¹⁸ and the further insights it is likely to provide into the design principles for IQC assembly. A simpler system is

also likely to be easier to realize experimentally (although DNA nanotechnology provides impressive examples of assembly from many building blocks¹⁹). For the BCI 5P system, we first noticed that the degree of incorporation of the yellow and purple particles was low (Extended Data Fig. 6), so we then ran an assembly simulation with just the red, blue and green particles; this again led to an IQC. Secondly, as the triacontahedron is stabilized by both red-green and green-green interactions, next we removed the patches mediating the green-green interactions; these changes did not hinder the IQC formation. Finally, we considered removing the red particles altogether, the inner shell of the cluster now just being a dodecahedron; again this still led to an IQC. One particularly noteworthy feature of this binary IQC-forming system is that both particles have four patches with an approximately tetrahedral geometry.

For the PI QC, the main modification that we considered was whether the red particles that formed the dodecahedral core of the cluster building blocks were necessary. A binary system of blue and green particles still reliably formed an IQC.

Finally, we considered whether the torsional components of the potentials were necessary for IQC formation. These control the relative orientations of two interacting particles and hence help propagate the global orientational order. Previous work on the formation of periodic crystals from patchy particles has shown that for more complex crystals there is often sufficient specificity within the matrix of patch-patch interactions for the target crystal to still reliably assemble without torsions, but for simpler crystals the absence of torsions may cause other polymorphs with similar local bonding patterns to compete with the target crystal^{16,21}. For the BCI 5P system, we found that the interactions between the red and green particles did not need torsions for the triacontahedra to form, but that without the torsional component the blue matrix particles had a tendency to phase separate, forming periodic polymorphs (see Supplementary Information). Similarly, the BCI 2P system was unable to assemble into an IQC without torsions. By contrast, the specificity in the PI designs precludes the possibility of a competing one-component crystal and both PI systems were able to reliably assemble into IQCs without torsions. All these successful simplifications are summarized in Fig. 4a,b and the diffraction patterns for all IQC-forming systems are shown in Extended Data Figs. 2 and 5. This exercise confirms both the modest number of assembly rules required to produce IQCs and the remarkable robustness of the IQC assembly. Note that the simulations of these systems always formed IQCs with no competing structures

150 ever being observed.

151 Structural and dynamic behaviour

152 Further insights into the nature of the ordering in the IQCs can be obtained by analysing
153 the structural and dynamical properties of the formed quasicrystals. First, we consider their
154 structure. The different roles each particle plays can be better seen by splitting up the
155 contributions to the BOODs by bond type (Extended Data Fig. 8). For example, in the
156 BCI 2P system, the green-green bonds are oriented along the two-fold axes, the green-blue
157 bonds along the three-fold axes and the blue-blue bonds along the five- and three-fold axes.
158 The BOODs are consistent with the symmetry of the particles; as illustrated in Extended
159 Data Fig. 8e,f the geometry of all particles is such that when appropriately oriented all
160 patches point along the rotation axes of the I_h point group. It is also interesting to examine
161 the coordination behaviour (Fig. 2c). The number of fully-bonded particles in the three
162 BCI systems is similar being about 60–70%, which is a bit lower than the ideal IQC (70%)
163 and significantly lower than the 3/2 approximant ($\sim 85\%$). For the PI 3P systems, this
164 figure is only 40–50% (Fig. 3c); this is partly because the blue particles have a particularly
165 low probability of being fully bonded. The blue particles both surround and bond to the
166 dodecahedra of red particles, but also form part of the inter-cluster matrix; in the latter
167 role the patches responsible for the blue-red interactions are unused. The fraction of fully-
168 coordinated particles, hence rises to approximately 60% in the PI 2P system.

169 The above results again emphasise that, due to the inherent frustration in packings with
170 icosahedral symmetry, global icosahedral order cannot be achieved with a small number of
171 particles without inevitable departures from maximal bonding. This feature probably ex-
172 plains why IQCs have never been observed for covalently-bonded material. For example,
173 although there are many materials based on tetrahedral coordination, IQCs like those as-
174 sembled from the BCI 2P system likely have too many dangling bonds for them to be stable
175 in a covalent material.

176 This also raises the question of whether the IQCs, as well as clearly being kinetically
177 favoured, are also ever thermodynamically most stable. For the BCI 5P system we can
178 compare the IQC to the 3/2 approximant. The 3/2 approximant will be lower in energy
179 because $\sim 85\%$ of the particles are fully bonded. However, the quasicrystal will have a

greater configurational entropy that stems from the variety of environments that particles can adopt both in terms of missing bonds and certain particles having patches that can bind to multiple other particles. We performed direct coexistence simulations²² to attempt to determine whether the 3/2 approximant or the IQC had a higher melting point for the BCI 5P system (see Supplementary Information). Although these simulations were not able to provide a conclusive answer, they showed that the two structures had very similar stability.

The aperiodicity of QCs also has consequences for their dynamic behaviour. Besides the phonon modes observed in usual crystals, QCs exhibit a second class of excitations called phasons that consist of local rearrangements of the atoms that change the local structure to a new configuration with almost the same energy and thus allow particle diffusion. One could imagine that such diffusion might be difficult for our patchy-particle systems due to the specificity and directionality of the bonding, particularly for those particles at the centres of clusters. The van Hove correlation functions depicted in Figs. 2d, 3f and Extended Data Figs. 9 and 10 show that the particle hops exhibit icosahedral symmetry, but with diffusion most prominent for the blue matrix particles in the BCI systems and the green matrix particles in the PI systems. Hence, the cluster centres are relatively immobile.

Possible experimental realization: DNA origami

An important question is, of course, whether such particle designs could be realized experimentally. Although there has been much progress in making colloids with “patchy” directional interactions^{23–25}, equivalents of these particles are probably most easily realizable using polyhedral DNA origami²⁶ with specific interactions between vertices. Such origamis have been recently used to make a number of periodic crystals²⁷. We explored the feasibility of this approach by designing DNA origami particle equivalents of a slightly-modified version of the BCI 2P system that is also able to form an IQC. Each origami has a tetrahedral core with arms protruding from each vertex at the end of which are short single-stranded DNA “sticky ends” that facilitate specific inter-origami binding (Fig. 4c). Simulations of a 70-particle icosahedral cluster of such origamis confirm that realizing IQCs with DNA origami is a realistic prospect. Such IQCs could be loaded with nanoparticles inside each tetrahedron²⁸ and would be excellent candidate materials for photonic applications due to their predicted almost spherically symmetric band gaps²⁹.

The rational design strategy that we have presented here should also be generalizable to quasicrystals with other symmetries. This raises the prospect of not only designing soft-matter quasicrystals with say octagonal and decagonal symmetries for the first time, but also realizing symmetries never previously achieved — a heptagonal quasicrystal would be a particularly attractive target³⁰.

REFERENCES

- ¹Shechtman, D., Blech, I., Gratias, D. & Cahn, J. W. Metallic phase with long-range orientational order and no translational symmetry. *Phys. Rev. Lett.* **53**, 1951–1953 (1984).
- ²Takakura, H., Gómez, C. P., Yamamoto, A., Boissieu, M. D. & Tsai, A. P. Atomic structure of the binary icosahedral Yb-Cd quasi-crystal. *Nat. Mater.* **6**, 58–63 (2007).
- ³Zeng, X. *et al.* Supramolecular dendritic quasicrystals. *Nature* **428**, 157–160 (2004).
- ⁴Haji-Akbari, A. *et al.* Disordered, quasicrystalline and crystalline phases of densely packed tetrahedra. *Nature* **462**, 773–777 (2009).
- ⁵Dotera, T. Quasicrystals in soft matter. *Isr. J. Chem.* **51**, 1197–1205 (2011).
- ⁶Dotera, T., Oshiro, T. & Ziherl, P. Mosaic two-length scale quasicrystals. *Nature* **506**, 208–211 (2014).
- ⁷Savitz, S., Babadi, M. & Lifshitz, R. Multiple-scale structures: from Faraday waves to soft-matter quasicrystals. *IUCrJ* **5**, 247–268 (2018).
- ⁸Subramanian, P., Archer, A. J., Knobloch, E. & Rucklidge, A. M. Three-dimensional icosahedral phase field quasicrystal. *Phys. Rev. Lett.* **117**, 075501 (2016).
- ⁹Engel, M., Damasceno, P. F., Phillips, C. L. & Glotzer, S. C. Computational self-assembly of a one-component icosahedral quasicrystal. *Nat. Mater.* **14**, 109–116 (2015).
- ¹⁰Damasceno, P. F., Glotzer, S. C. & Engel, M. Non-close-packed three-dimensional quasicrystals. *J. Phys: Condens. Matter* **29**, 234005 (2017).
- ¹¹Reinhardt, A., Schreck, J. S., Romano, F. & Doye, J. P. K. Self-assembly of two-dimensional binary quasicrystals: A possible route to a DNA quasicrystal. *J. Phys.: Condens. Matter* **29**, 014006 (2016).
- ¹²Sadoc, J.-F. & Mosseri, R. *Geometric Frustration* (Cambridge University Press, Cambridge, 1999).
- ¹³Doye, J. P. K. & Wales, D. J. Structural consequences of the range of the interatomic

- potential: A menagerie of clusters. *J. Chem. Soc., Faraday Trans.* **93**, 4233–4244 (1997).
- ¹⁴Dmitrienko, V. & Kléman, M. Tetrahedral structures with icosahedral order and their relation to quasi-crystals. *Crystallogr. Rep.* **46**, 527–533 (2001).
- ¹⁵Liu, L., Li, Z., Li, Y. & Mao, C. Rational design and self-assembly of two-dimensional dodecagonal quasicrystals. *J. Am. Chem. Soc.* **141**, 4248–4251 (2019).
- ¹⁶Tracey, D. F., Noya, E. G. & Doye, J. P. K. Programming patchy particles to form complex ordered structures. *J. Chem. Phys.* **151**, 224506 (2019).
- ¹⁷Janot, C. *Quasicrystals. A primer* (Oxford University Press, Oxford, 2002).
- ¹⁸Cadamartiri, L. & Bishop, K. J. M. Programmable self-assembly. *Nat. Mater.* **14**, 2–9 (2015).
- ¹⁹Liu, W., Halverson, J., Tian, Y., Tkachenko, A. V. & Gang, O. Self-organized architectures from assorted DNA-framed nanoparticles. *Nat. Chem.* **8**, 867–873 (2016).
- ²⁰Snodin, B. E. K. *et al.* Introducing improved structural properties and salt dependence into a coarse-grained model of DNA. *J. Chem. Phys.* **142**, 234901 (2015).
- ²¹Zhang, Z., Keys, A. S., Chen, T. & Glotzer, S. C. Self-assembly of patchy particles into diamond structures through molecular mimicry. *Langmuir* **21**, 11547–11551 (2005).
- ²²Vega, C., Sanz, E., Abascal, J. L. F. & Noya, E. G. Determination of phase diagrams via computer simulation: methodology and applications to water, electrolytes and proteins. *J. Phys.: Condens. Matter* **20**, 153101 (2008).
- ²³Glotzer, S. C. & Solomon, M. J. Anisotropy of building blocks and their assembly into complex structures. *Nat. Mater.* **6**, 557–562 (2007).
- ²⁴Li, W. *et al.* Colloidal molecules and patchy particles: complementary concepts, synthesis and self-assembly. *Chem. Soc. Rev.* **49**, 1955–1976 (2020).
- ²⁵Xiong, Y. *et al.* Three-dimensional patterning of nanoparticles by molecular stamping. *ACS Nano* **14**, 6823–6833 (2020).
- ²⁶Veneziano, R. *et al.* Designer nanoscale DNA assemblies programmed from the top down. *Science* **352**, 1534 (2016).
- ²⁷Tian, Y. *et al.* Ordered three-dimensional nanomaterials using DNA-prescribed and valence-controlled material voxels. *Nat. Mater.* **19**, 789–796 (2020).
- ²⁸Ma, N. *et al.* Directional assembly of nanoparticles by DNA shapes: Towards designed architectures and functionality. *Top. Curr. Chem.* **378**, 36 (2020).
- ²⁹Man, W., Megens, M., Steinhardt, P. J. & Chaikin, P. M. Experimental measurement of

the photonic properties of icosahedral quasicrystals. *Nature* **436**, 58–63 (2005).
³⁰Steurer, W. Boron-based quasicrystals with sevenfold symmetry. *Philos. Mag.* **87**, 2707–
2712 (2007).

FIG. 1. **From ideal quasicrystal to patchy-particle design.** **a**, Target ideal BCI QC structure and **b**, its $3/2$ rational approximant (obtained by the cut-and-project method). **c**, Geometry of the local environments in the ideal QC organized in classes that are characterized by the same local geometry but with some dangling bonds. Those local environments also present in the $3/2$ rational approximant are shadowed in red. **d**, Structure of the icosahedral clusters forming the IQC. The inner shell is a 32-particle triacontahedra, which is surrounded by a shell of 50 four-patch particles. **e**, Model patchy particles used for the assembly of the BCI QC.

FIG. 2. **Assembly of a body-centred icosahedral quasicrystal.** **a**, The BCI 5P model (Fig. 1e) assembles into a cluster with a rather irregular surface in coexistence with the gas phase. The cluster has been bisected to reveal its inner structure. (See Extended Data Fig. 1 for further views of the IQC.) The BOOD shown in the upper right corner exhibits icosahedral symmetry. **b**, Diffraction patterns along five-fold (top) and two-fold (bottom) symmetry axes. **c**, Fraction of particles with a given number of dangling bonds for the different BCI systems. **d**, van Hove autocorrelation function of the particle positions measured after one million of MC cycles for the BCI 5P model.

FIG. 3. **A patchy-particle primitive icosahedral quasicrystal.** **a**, 152-particle icosahedral cluster identified in the ideal PI QC and in its $8/5$ rational approximant. **b**, Model particles for the assembly of this cluster. **c**, Snapshot of an IQC assembled from a low-density fluid composed of green, red and blue particles, aligned along a five-fold symmetry axis, along with the BOOD. (See Extended Data Fig. 4 for further views of the IQC.) **d**, Diffraction patterns along the five-fold and two-fold axes. **e**, Fraction of particles with a given number of dangling bonds for the different PI systems. **f**, van Hove autocorrelation function of the particle positions measured after one million of MC cycles for the PI 3P model.

FIG. 4. **Minimal quasicrystal-forming systems.** Simplification of the **a** BCI and **b** PI QC model systems. The figure depicts the particle types used for each system and illustrates the relationships between them by the differences in their icosahedral clusters (WT: with torsions; NT: no torsions). **c**, DNA origami, as modelled by oxDNA²⁰, that realize the BCI 2P patchy particles, and an assembly of 70 such origami into the basic icosahedral cluster (this structure contains approximately half a million nucleotides).

METHODS

Generation of target ideal IQCs

Ideal IQCs were generated by the cut-and-project method, i.e. by projection of irrational cuts of periodic structures in a higher dimensional space onto the physical space. In particular, IQCs become compatible with a periodic lattice in 6D space. This higher-dimensional space can be separated into two orthogonal subspaces, the parallel (or physical) and perpendicular spaces. IQCs are obtained by projecting the 6D lattice positions that fall within a region of the perpendicular space (the atomic surface or occupation domain) onto the physical space. Three different 6D hypercubic lattices are compatible with icosahedral symmetry, namely, the simple cubic or primitive (P), the body-centred (BC) and the face-centred (FC). The occupation domain defined by the perpendicular space must have the same point group symmetry as the IQC. Thus, the structure of an ideal IQC is uniquely defined by the 6D lattice and occupation domain.

Using this procedure we generated two target ideal IQCs. The first one was based on the 6D BC lattice with a dodecahedron occupation domain. The second target IQC was built from a 6D primitive lattice. Rather than taking the canonical choice for the occupation domain (which corresponds to a triacontahedron), we decided to use instead a dodecahedron occupation domain. By using this occupation domain we obtained an IQC with less local environments and smaller differences in bond lengths than with the canonical choice.

Besides generating the IQC, we also produced some of the lower order rational approximants, as these also help to identify the relevant local environments for the model design. Rational approximants can be also obtained using the higher-dimensional approach by changing the orientation of the acceptance domain with respect to parallel space. Mathematically, this is done by replacing τ (the golden ratio) by the approximation given by the ratio of two successive Fibonacci numbers q/p when defining the perpendicular space. The lattice constant of the approximant unit cell increases by a factor of τ and the number of atoms by τ^3 for successive q/p approximants (1/0, 1/1, 2/1, 3/2, 5/3, 8/5,...).

Full mathematical details are given in Section S1A of the Supplementary Information.

Environment analysis

Once the target ideal IQC and its lower rational approximants were generated, model systems were built based on the local environments found in these structures. The first step is to define the cutoff distance below which two neighbour particles are considered to form a bond. The pair distribution function (PDF) of the ideal BCI QC exhibits three first peaks at distances within 1.0-1.1548, followed by three other peaks at distances between 1.618-1.868 (Extended Data Fig. 6a). Thus, adopting the convention that the first three peaks belong to the first coordination shell appears as a natural choice. For simplicity, differences in bond lengths within the first coordination shell ($\sim 15\%$) were ignored while designing the BCI model system. Next the atomic positions in the target structure were classified according to their number of bonds and the angles formed between the central particle and its neighbours. The local environments of the ideal BCI QC and its rational approximant are discussed in the main text and are shown in Fig. 1, with further details in Table S1 of the Supplementary Information.

For the ideal PI QC, the PDF exhibits three peaks at distances within 0.80-1.31, followed by three other peaks at distances within 1.72–2.01 (Extended Data Fig. 7a). In this case, the cutoff distance used to define the bonds includes only the two first peaks. Including the third peak leads to the formation of redundant bonds linking particles that have two common neighbours belonging to the first two peaks in the PDF. Differences between the two bond lengths in the first coordination shell are too big ($\sim 30\%$) to be simply ignored, and are taken into account in the model design. Using this choice for the first coordination shell, we found that there are fourteen local environments in the ideal IQC with coordination numbers ranging from four to twenty, that are reduced to twelve in the $8/5$ approximant (See Table S2 in the Supplementary Information). Inspection of the structure of the ideal PI QC and its $8/5$ approximant (see Extended Data Fig. 3) reveals that there is a common building block to both structures, consisting of an inner dodecahedral shell formed by six-coordinate particles, surrounded by a three-layer shell formed by five- and eight-coordinate particles (see Figure 3a). This shell cluster contains only three local environments, thus only three particle types are needed for its assembly (green, red and blue particles defined in Table S6). Bond distances within the inner dodecahedral shell (formed by red particles) correspond to the first peak in the PDF and are substantially shorter than the remaining

bond lengths. This was taken into account by adjusting the model parameters so that the red-red bond distance is shorter than the remaining bonds. Environments with high coordination correspond to particles enclosed in the central dodecahedral cage of the shell cluster and its incomplete versions that appear in the IQC. These particles are not needed to build the structure and thus are simply neglected. The remaining local environments form a matrix that surround and merge the icosahedral shell clusters and, given that they were not necessary for the assembly of the BCI QC, they were also disregarded in this case.

Patchy-particle potential

The interactions between particles are described using the same patchy-particle model as in Refs. 16 and 32. In this pair potential, the interaction is described by a Lennard-Jones repulsive core and an attractive tail modulated by angular and torsional dependent functions. The angular modulation term has a Gaussian form and is a measure of how directly two patches point at each other. The standard deviation of the Gaussian σ_{ang} is a measure of the angular width of the patch.

The torsional modulation term describes the variation in the potential as either of the particles is rotated about the interparticle vector. It has a Gaussian form that is centred at the preferred torsional angle. The parameter σ_{tor} is a measure of the torsional specificity of the interaction. In order to capture the symmetry of an environment, more than one preferred torsional angle can be defined.

The torsional interactions facilitate the propagation of long-range orientational order. In practice, to realize a torsionally-specific interaction requires a “structured” patch. This is naturally provided by the protein-protein interfaces in protein complexes, but has also been achieved using DNA-origami mediated interactions between colloids³³. The interactions between the six-helix bundle arms of the DNA origamis that we propose as analogues of the patchy particle are also torsionally specific.

We use $\sigma_{\text{tor}} = 2\sigma_{\text{ang}}$ throughout, and unless otherwise stated use $\sigma_{\text{ang}} = 0.3\text{rad}$ (the effects of varying σ_{ang} are described in Section S4D of the Supplementary Information). We use σ_{LJ} (the distance at which the Lennard-Jones potential is zero) as our unit of length, and the Lennard-Jones well depth ε_{LJ} as our unit of energy. Temperatures are given in reduced form, $T^* = k_B T / \varepsilon_{\text{LJ}}$. The precise mathematical form of the potential is described in Section

S1B of the Supplementary Information.

The properties of the patchy interactions (the patch directions, specificity, parameters of the torsional potentials) for the BCI 5P model and PI 3P model are defined based on the environments in the approximant unit cell. For patches involved in interactions with multiple other types of patches (i.e. those not related by symmetry), the torsional interactions are only applied to one of the interactions. All the other models are derived from the BCI 5P and PI 3P models. The details of each model are fully tabulated in the Supplementary Information.

Patchy-particle simulations

The assembly behaviour of the model patchy-particle systems was studied by means of Monte Carlo (MC) simulations in the NVT ensemble. Simulations were performed with a bespoke GPU parallel MC code. The simulation box is partitioned in cubic cells (of size equal or larger than the interaction range) using a checkerboard decomposition³⁴, so that multiple MC moves can be performed simultaneously in a subset of cells. Following the extension proposed in Ref. 34, 27 GPU threads per cell were used, each thread computing the energy of the old and new configurations after a MC move in the central and the 26 surrounding cells. In this implementation, a larger number of GPU threads are used, reducing the system size for which the GPU code starts to perform better than the CPU code.

Simulations were performed in a cubic box containing about 20 000 particles, initially randomly distributed, at a low density, typically $\rho = 0.1 \sigma_{LJ}^{-3}$, at a temperature at which nucleation occurs via a single solid nucleus in reasonable computational times. The composition of the fluid of particles was set to the same proportion as that found in the target IQC. At these conditions, the system forms a roughly spherical cluster that is in coexistence with a low-density gas. Thus, we avoid the appearance of defects caused by the incommensurability of the grown IQC with the periodic simulation box.

Once a sufficiently large solid cluster is obtained (of about 14 000–16 000 particles), this crystal seed is immersed in a larger simulation box containing a fluid of particles at low density with about 100 000 particles, tweaking the fraction of each particle type to match that of the assembled cluster if needed. Simulations in these bigger systems are performed at a temperature somewhat higher than in the nucleation simulations to avoid the assembly

of a second solid nucleus during the growth of the inserted quasicrystalline seed. Using this protocol we were able to grow aggregates with up to 60 000–70 000 particles. These simulations were continued over at least 2 million MC cycles (where a MC cycle is defined as 20 MC moves per cell) for measuring different structural and dynamical properties. The temperatures used in the nucleation and growth simulations for each system are given in Table S9.

Additional simulations at fluid compositions deviating significantly from the preferred composition of the quasicrystals are also reported in Section S4B of the Supplementary Information. These confirmed that the reported IQCs are able to robustly assemble from fluid mixtures with a wide range of compositions.

Analysis

The structure of the aggregates formed in the patchy-particle simulations was determined by analyzing several structural properties. Long trajectories of about 2 million MC cycles were used for the analysis. The solid cluster was identified by using a cluster search algorithm³⁵ with the convention that two neighbouring particles form a bond if their interaction energy is lower than $-0.15 \varepsilon_{\text{LJ}}$. The trajectories were aligned using the centre of mass of the cluster as the coordinate origin and by minimizing the mean square displacement of those particles belonging to the core of the cluster. Radial density profiles were used to identify the cluster core as the region in which the density remains roughly constant. The orientational order of the cluster was initially analyzed by measuring the bond-orientational order diagram (BOOD). In these diagrams the nearest coordination shell of each particle is plotted on a unit sphere. This sphere was then projected onto a plane perpendicular to the symmetry axis using the area-preserving Lambert projection. The cutoff distance of the first coordination shell was taken as that of the first minimum in the radial distribution function. Calculation of individual BOODs for each bond type (involving any combination of two interacting particle types) was used to understand the structural role of each bond type. Average diffraction patterns were then calculated by orienting the clusters along the two-, three- and five-fold rotational symmetry axes. Further structural information was obtained by measuring the average composition and average number of dangling bonds per particle type.

Single particle motion in the assembled IQCs was quantified by measuring the van Hove autocorrelation function $G(\mathbf{r}, t)$ of the particle positions³⁶:

$$G(\mathbf{r}, t) = \frac{1}{N} \sum_{i=1}^N \langle \delta [\mathbf{r} - \mathbf{r}_i(t) + \mathbf{r}_i(t=0)] \rangle \quad (1)$$

This function measures the displacement of individual particles from their initial positions at selected times t . In crystals without defects particles remain at distances less than the size of the particle. However, in IQCs phason flips allow larger displacements of the particles. van Hove autocorrelation functions were measured after 1 million MC cycles using trajectories of 2–10 million MC cycles and then projected onto planes perpendicular to the five-fold symmetry axes. Measurement of separate van Hove autocorrelation functions for each particle type reveals that the mobility of the different particle types can differ significantly.

The van Hove autocorrelation functions were measured at the same temperature as that used for the cluster growth (specific temperatures used for each model system are provided in the Supplementary Information, Table S9). For the BCI 5P model, the van Hove function was also calculated at an additional higher temperature, namely, $T^*=0.096$. The results are provided in the Supplementary Information, Fig. S2. As expected, at higher temperatures particle mobility is higher, but the main features of the van Hove plots remain the same.

DNA origami modelling

To model DNA origamis and their assemblies, we use the oxDNA model²⁰ and simulation code³⁷. OxDNA is a coarse-grained model of DNA at the nucleotide level, which has been designed to accurately capture the structure, mechanics and thermodynamics of DNA and its assemblies. It has been extensively used to model DNA origami. For example, it accurately reproduces the most detailed experimental origami structure in the literature that was obtained by cryo-electron microscopy^{38,39}. The generated DNA origami and their assemblies were simulated by molecular dynamics in the canonical ensemble.

To design DNA origami particles that are equivalents of the BCI 2P patchy particles, we first used TALOS⁴⁰ to create the design for the central tetrahedron. This is not a regular tetrahedron but has edge lengths that lead to the required inter-patch angles. caDNAno⁴¹

is then used to create six-helix bundle extensions out from each vertex with short single-stranded sticky ends to mediate the interparticle interactions. These sticky-end interactions can both be specific and allow control of the preferred torsional angle. This design, however, does not allow inter-origami interactions that exactly match those of the BCI 2P patchy particles, so two modifications to the patchy-particle design had to be introduced. First, an origami arm cannot both bind to a copy of itself and an arm on a different particle that is not self-interacting. Thus, we removed the self-interactions between the P_B^4 patches. Second, the interactions between two six-helix bundle arms can either have a single preferred torsional offset angle, or three equivalent angles. Thus, we increased the number of possible offset angles for patches P_B^{1-3} from two to three. We first checked that patchy particles with these modifications (BCI 2P-mod) could still form an IQC. They did, as evidenced by the diffraction patterns in Extended Data Fig. 2.

To simulate the origamis using oxDNA we converted the caDNAno designs into oxDNA configurations using tacoxDNA⁴². We then placed the requisite number of copies of the two origamis in approximately the correct geometry to form the icosahedral 70-origami cluster. We initially simulated the system with artificial forces added that pulled the sticky ends together to achieve rapid assembly of the cluster. These forces were then removed for the final simulations of the complete cluster. The cluster contains 532 440 nucleotides. Further details of the origami designs can be found in the Supplementary Information.

The DNA origami design process outlined here can potentially be extended to other patchy-particle designs. Firstly, different numbers of patches can be achieved by having different polyhedra at the centres of the origami. Secondly, fine-tuning of the offset angles could be achieved by introducing twist into the six-helix bundle arms by changing the number of nucleotides between some junctions from their preferred values⁴³. Thirdly, the arm lengths can be varied to give different bond lengths for particular interactions.

DATA AVAILABILITY

Final configurations of all systems, along with scripts for their viewing, are available from the Oxford University Research Archive (<https://doi.org/10.5287/bodleian:R8eMnrapg>). Source data are provided with this paper.

CODE AVAILABILITY

The patchy-particle Monte Carlo simulation code is available from https://github.com/evanoya/MC_GPU. The simulation code incorporating the oxDNA model is available from <https://sourceforge.net/projects/oxdna/>.

³¹Steurer, W. & Deloudi, S. *Crystallography of quasicrystals: concepts, methods and structures* (Springer Series in Material Science, 2009).

³²Wilber, A. W., Doye, J. P. K., Louis, A. A. & Lewis, A. C. F. Monodisperse self-assembly in a model with protein-like interactions. *J. Chem. Phys.* **131**, 175102 (2009).

³³Ben Zion, M. Y. *et al.* Self-assembled three-dimensional chiral colloidal architecture. *Science* **358**, 633–636 (2017).

³⁴Anderson, J. A., Jankowski, E., Grubb, T. L., Engel, M. & Glotzer, S. C. Massively parallel Monte Carlo for many-particle simulations on GPUs. *J. Comput. Phys.* **254**, 27–38 (2013).

³⁵Rapaport, D. C. *The Art of Molecular Dynamics Simulation* (Cambridge University Press, Cambridge, 2004).

³⁶Engel, M., Umezaki, M., Trebin, H.-R. & Odagaki, T. Dynamics of particle flips in two-dimensional quasicrystals. *Phys. Rev. B* **82**, 134206 (2010).

³⁷Rovigatti, L., Šulc, P., Reguly, I. Z. & Romano, F. A comparison between parallelization approaches in molecular dynamics simulations on GPUs. *J. Comput. Chem.* **36**, 1–8 (2015).

³⁸Bai, X.-C., Martin, T. G., Scheres, S. H. W. & Dietz, H. Cryo-EM structure of a 3D DNA-origami object. *Proc. Natl. Acad. Sci. USA* **109**, 20012–20017 (2012).

³⁹Snodin, B. E. K., Schreck, J. S., Romano, F., Louis, A. A. & Doye, J. P. K. Coarse-grained modelling of the structural properties of DNA origami. *Nucleic Acids Res.* **47**, 1585–1597 (2019).

⁴⁰Jun, H. *et al.* Automated sequence design of 3D polyhedral wireframe DNA origami with honeycomb edges. *ACS Nano* **13**, 2083–2093 (2019).

⁴¹Douglas, S. M. *et al.* Rapid prototyping of 3D DNA-origami shapes with caDNAno. *Nucleic Acids Res.* **37**, 5001–5006 (2009).

⁴²Suma, A. *et al.* TacoxDNA: a user-friendly web server for simulations of complex DNA structures, from single strands to origami. *J. Comput. Chem.* **40**, 2586–2595 (2019).
⁴³Dietz, H., Douglas, S. M. & Shih, W. M. Folding DNA into twisted and curved nanoscale shapes. *Science* **325**, 725–730 (2009).

ACKNOWLEDGMENTS

We are grateful for financial support from the Agencia Estatal de Investigación and the Fondo Europeo de Desarrollo Regional (FEDER) under grant Nos. FIS2015-72946-EXP(AEI) and FIS2017-89361-C3-2-P(AEI/FEDER,UE) (E.G.N) and the Croucher Foundation (C.K.W). We acknowledge the use of the University of Oxford Advanced Research Computing (ARC) facility and the Cambridge Service for Data Driven Discovery (CSD3).

AUTHOR CONTRIBUTIONS

E.G.N. and J.P.K.D. designed the research; E.G.N. wrote the MC code used for the simulations of systems of patchy particles and built the ideal IQC and approximants used as target structures; E.G.N., C.K.W. and P.L. performed the patchy-particle simulations and analyzed the data; C.K.W. designed the DNA-origami particles and performed the simulations on these systems. All the authors discussed the results. J.P.K.D., E.G.N. and C.K.W wrote the article.

ADDITIONAL INFORMATION

Supplementary Information is available for this paper.

COMPETING FINANCIAL INTEREST

The authors declare no competing interests.

FIG. 1. (Extended Data) **Structure of the body-centred icosahedral quasicrystals.** Projections of the BCI 5P and 2P IQCs along the five-fold axis (top), three-fold axis (middle) and two-fold axis (bottom). In the three-fold axis, self-similar triangular motifs follow a $1:\tau:\tau^2:\tau^3$ scaling that is a characteristic of IQCs.

FIG. 2. (Extended Data) **Body-centred IQC diffraction patterns.** Comparison of the diffraction patterns of the ideal BCI QC and its $3/2$ approximant, with those of the assembled IQCs using the BCI 5P, 3P, 2P and 2P-mod models. All four assembled systems have diffraction patterns with clear five-fold symmetry confirming their IQC character. By contrast, the diffraction pattern of the approximant when viewed along the pseudo-fivefold axis shows clear deviations from five-fold symmetry. The diffraction patterns of the BCI 5P and 3P models most closely resemble those of the ideal IQC; the indexing of all peaks with a BCI indexing scheme is detailed in Section S4E of the Supplementary Information. The diffraction patterns for the BCI 2P and 2P-mod models exhibit additional features, particularly along the two-fold and five-fold axes; these include both diffuse scattering and extra weak peaks that cannot be indexed in a BCI indexing scheme (see Supplementary Information).

FIG. 3. (Extended Data) **An ideal primitive icosahedral quasicrystal.** **a**, PI QC model with a dodecahedral occupation domain viewed along the five-, three- and two-fold rotational axes. In the top row, only the red and those blue particles that are bonded to red particles are shown; these views clearly show that not all the clusters are perfect. In the lower row, all particles are shown. The yellow particles form an additional shell around the icosahedral cluster depicted in Fig. 3(a) and all other matrix particles are coloured pink. **b**, Views of the $8/5$ rational approximant along the psuedo-five-, three- and two-fold rotational axes.

FIG. 4. (Extended Data) **Structure of the primitive icosahedral quasicrystals.** Projections of the PI 3P WT and 2P WT models along the five-fold axis (top), three-fold axis (middle) and two-fold axis (bottom). In the three-fold axis, self-similar triangular motifs follow a $1:\tau:\tau^2:\tau^3$ scaling that is a characteristic of IQCs.

FIG. 5. (Extended Data) **Primitive IQC diffraction patterns.** Comparison of the diffraction patterns of the ideal PI QC and its $8/5$ approximant with those of the IQCs obtained from simulations. All four assembled systems have diffraction patterns with clear five-fold symmetry confirming their IQC character. By contrast, the diffraction pattern of the approximant when viewed along the pseudo-fivefold axis shows clear deviations from five-fold symmetry. Despite the assembled systems being simpler than the ideal IQC in terms of the number of environments, the diffraction patterns are very similar to that for the ideal IQC with the patterns along the two-fold axis showing the most differences. The PI 2P diffraction patterns could be satisfactorily indexed with a PI indexing scheme, but the more well-resolved PI 3P patterns have additional weak peaks that require a face-centred icosahedral (FCI) indexing scheme with a hypercubic lattice parameter that is double that for the PI indexing scheme, indicating some superstructural ordering (see Section S4E of the Supplementary Information). The diffraction patterns for the systems with and without torsions show no clear differences, confirming their structural similarity.

FIG. 6. (Extended Data) **Structural analysis of the body-centred IQCs.** The properties of the BCI QCs obtained with the 5P, 3P and 2P models are compared to those of the ideal BCI QC and its $3/2$ rational approximant. **a**, Pair distribution functions (PDFs) evaluated considering only those particles within a sphere of radius $15\sigma_{LJ}$ centred at the centre of mass of the solid cluster. There is a good coincidence between the broadened (due to thermal motion) peaks for the assembled IQCs and the distances present in the ideal IQC consistent with their similar structure. The PDFs for the BCI 5P and 3P systems are essentially the same, with the differences from the BCI 2P system still being relatively small. **b**, Radial density. The bulk densities of the ideal IQC, the BCI 5P and 3P systems and the $3/2$ approximant are very similar, but with the BCI 2P being lower as expected due to the absence of the red particles. The radial density of the assembled systems decreases from its bulk value to zero over $10\text{--}15\sigma_{LJ}$ reflecting the rather irregular nature of the surface of the assemblies. **c**, Mole fraction of each particle type in the different structures. The incorporation of the yellow and purple particles into the BCI 5P assembly is much lower than for the ideal IQC. Also the fraction of red and blue particles in the BCI 5P and 3P assemblies is closer to that for the approximant than the ideal IQC. The BCI 2P system assemblies have a significantly increased fraction of green particles. **d-i**, Probability of the number of dangling bonds for each particle type **d-h** and considering all particle types **i**. The assembled IQCs show a greater number of dangling bonds for the blue matrix particles than the ideal IQC, whereas the ideal IQC has a greater number of dangling bonds for the red and green particles that form the triacontahedral clusters.

FIG. 7. (Extended Data) **Structural analysis of the primitive IQCs.** The properties of the PI QCs obtained with the 3P and 2P models with and without torsions are compared to those of the ideal PI QC. **a**, Pair distribution function (PDF), evaluated considering only those particles within a sphere of radius $15\sigma_{\text{LJ}}$ centred at the centre of mass of the the solid cluster. The peaks in the PDFs are consistent with the distances in the ideal IQC, even though the assembled systems do not have particles corresponding to many of the environments in the ideal IQC. The 2P system does not have the peak at $\sim 0.8\sigma_{\text{LJ}}$ that is due to the red-red bonds. **b**, Radial density. The bulk densities of the 3P systems are a bit lower than the ideal IQC with the 2P systems having a further lowered density due to the absence of red particles. **c**, Mole fraction of each particle type in the different structures. Note that in the ideal structure the mole fractions do not add to one, as there are additional local environments that are not included in this plot. Particularly noticeable is the much smaller number of red particles in the ideal IQC. **d-g**, Probability of the number of dangling bonds for each particle type **d-f** and considering all particle types **g**. The blue particles in the 3P systems have a particularly low probability of having no missing bonds, because when forming part of the inter-cluster matrix, they do not use their two patches that can only bond to the red particles that form the dodecahedral clusters; such particles contribute to the relatively large number of blue particles with two dangling bonds.

FIG. 8. (Extended Data) **Bond orientational order.** Contributions to the BOOD for the **a**, BCI 5P, **b**, BCI 2P, **c**, PI 3P WT and **d**, PI 2P WT QCs from the different patch-patch bonds types in these systems. For the BCI systems, the green-green and purple-purple bonds are directed along the two-fold axes, the blue-green and blue-purple along the three-fold axes, the blue-red, red-green, blue-yellow and yellow-purple along the five-fold axes, and the blue-blue can be directed along five-fold (bonds formed through patches 1 to 3) and three-fold (bonds formed by patch 4) axes. For the PI systems, the red-red bonds are directed along the two-fold axes, and the green-blue and red-blue along the three-fold axes. Thus, for the PI 2P WT the total BOOD only exhibits spots directed along the three-fold axes, whereas for the PI 3P WT there are also spots along the two-fold axes. Contributions to the BOODs calculated using a distance cutoff exhibit additional spots but always directed along the rotational axes of the I_h point group (Fig. S7 in the Supplementary Information). **e**, **f**, The relationship between the symmetry of the patchy particles and the I_h point group. All particles can be oriented so that their patch vectors point exclusively along the rotational axes of I_h . This is illustrated for the patchy particles in the **e**, BCI 5P and **f**, PI 3P models by depicting the direction of the patch vectors \mathbf{P}_i by circles (with the colours representing (one of) the particles with which they interact) on the surface of an icosahedron. The projections chosen are along the highest rotational axis of the particles. Edges on the back faces of the icosahedra are dashed and cyan. Similarly, for patch vectors on the back faces the colour shade is lighter and ringed in cyan rather than black. The BOODs in **a-d** are fully consistent with the particles being oriented in this way with respect to the global icosahedral order of the IQCs. Note also that the preferred torsional angles of each patch-patch interaction are those that ensure the propagation of this global orientational order.

FIG. 9. (Extended Data) **Dynamics of the body-centred IQCs.** van Hove autocorrelation functions for the simulated BCI QCs, evaluated at 1 million Monte Carlo cycles and considering only those particles within a radius of $20\sigma_{\text{LJ}}$, which corresponds to the interior of the cluster where the radial density is constant (Extended Data Fig. 6b). The majority of the particle mobility is associated with the blue matrix particles, whereas the red and green particles that form the inner shell of the icosahedral clusters have very limited mobility. The yellow particles in the 5P system are the most mobile but are only present at very low mole fraction.

FIG. 10. (Extended Data) **Dynamics of the primitive IQCs.** van Hove autocorrelation function for the simulated PI QCs, evaluated at 1 million Monte Carlo cycles and considering only those particles within a radius of $20\sigma_{\text{LJ}}$, which corresponds to the interior of the cluster where the radial density is constant (Extended Data Fig. 7b). Although the overall pattern shows clear five-fold symmetry, the peaks merge into each other more than for the BCI systems. This is partly because the size of the allowed hops is shorter. The green particles are the most mobile, and the red particles, which form the inner shell of the icosahedral clusters, are least mobile. It is also noticeable that without torsions, the 3P system has greater mobility, and that the 2P patterns are less well-defined, with the blue particle motion being close to isotropic.