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Three-periodic tilings and nets: face-transitive tilings and edge-transitive nets revisited

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Systematic generation of face-transitive tilings by size of Delaney–Dress symbol has recovered by dualization all the edge-transitive nets previously described and has led to the discovery of six new binodal edge-transitive nets which are described and illustrated.

1. Introduction

In the designed synthesis of crystalline materials by linking molecular building units (reticular chemistry, Yaghi *et al.*, 2003), nets with just one kind of edge (*edge-transitive*) play a pre-eminent role. Previously (Delgado Friedrichs *et al.*, 2003*a*,*b*, 2006), we described 20 uninodal (vertex-transitive) and 28 binodal nets of this kind. Of the last work, a prescient referee remarked that there was 'little smell of unsatisfactoriness, because of the fact that no proof of completeness is given'. Part of the problem is that we know in fact of infinite families of edge-transitive nets (Delgado-Friedrichs *et al.*, 2005) and we have somewhat arbitrarily chosen what we believe to be a finite subset of the 'most important' (in the context of reticular chemistry) nets that obey the conditions that (*a*) for uninodal nets in their most symmetric embeddings there are no intervertex distances shorter than the edge length or (*b*) for binodal nets similarly embedded there are no distances between unlike vertices that are shorter than the edge length.

The problem of systematically and exhaustively enumerating nets is a very difficult one and rapidly leads to explosions in the number of candidates (*e.g.* Bader *et al.*, 1997; Treacy *et al.*, 2004). One of the most fruitful methods has been the enumeration of periodic tilings, and hence the nets they carry, using the methods of combinatorial tiling theory (Delgado-Friedrichs *et al.*, 1999).

Periodic tilings can be encoded in Delaney–Dress symbols (here D-symbols) introduced by Dress (1984, 1987) inspired by earlier work by Delaney (1980). D-symbols have proven invaluable in many areas of tiling theory as they can be systematically generated and those associated with tiling of Euclidean space explicitly recognized (Delgado-Friedrichs, 2001). A tiling can be divided up into fundamental simplices called chambers and the D-symbol specifies how these are joined to form the tiling. The number of separate kinds (*i.e.* not symmetry-related) of such chambers is known as the size of the symbol and we refer to it as the D-size.

An important paper (Dress *et al.*, 1993) that provided some inspiration for the present work showed that, for tilings of space by conventional polyhedra (*i.e.* those with 3-connected planar graphs), there are just seven topological types of face-transitive tiling. In the dual of a three-dimensional tiling, the correspondence is vertex ↔ tile and edge ↔ face so the duals of these structures are edge transitive. They carry the well known nets with symbols **pcu**, **fcu**, **sod**, **reo**, **crs** and **flu**.[1] Clearly this approach does not lead to all edge-transitive nets; familiar structures such as the net (**dia**) of diamond are missing. The reason is that the tiles in tilings for most nets are not polyhedra *sensu stricto* but are cages with divalent vertices (see *e.g.* Delgado Friedrichs *et al.*, 2003*a*). Accordingly, in this work we have undertaken systematic enumeration of edge-transitive tilings; these will carry edge-transitive nets.

2. Enumeration methods

A net may admit an infinite number of tilings but tilings with the same symmetry (isomorphism group) of the net are limited – indeed in many cases unique – so we limit tilings to those of this sort which we term proper.

In order to generate edge-transitive tilings, it is easier to think in terms of the dual problem, namely generating face-transitive tilings. These two problems are completely equivalent and, indeed, a tiling and its dual have D-symbols of the same size which can be transformed into each other in a trivial way. Given a face-transitive tiling, we can then directly determine the net carried by its dual tiling by putting a node inside each tile and connecting two nodes whenever the corresponding tiles share a face.

We have adapted the approach of Dress *et al.* (1993) which distinguishes three types of face-transitive tilings. The first has one kind of tile and one kind of face with respect to the site symmetry of the tile. The second type also has one kind of tile, but two kinds of face with respect to the site-symmetry group. These two kinds can be imagined as the two sides of a coin insofar as, when tiles are assembled to form a tiling, a face of the first kind always has to be matched with a face of the second kind (*i.e.* head to tail). The third type of tiling has two

[1] The reader will have noticed that we list only six nets; this is because two of the relevant tilings (the duals of numbers 4 and 80 in Table 2 of Dress *et al.*, 1993) carry the same net (**fcu**). Symbols for nets are those in the RCSR database of nets at http://rcsr.anu.edu.au.

Table 1
Edge-transitive nets retrieved in this study listed by size of the Delaney–Dress symbol (D-symbol) of the proper tiling with smallest size.

The three-letter symbols are the RCSR (http://rcsr.anu.edu.au/) symbols.

D-symbol size	Uninodal	Binodal
1	**pcu**	
2	**bcu**, **dia**, **fcu**, **nbo**	**flu**
3	**reo**, **sod**	
4	**crs**, **hxg**	**ftw**
6	**acs**	
8	**rhr**	**bor**, **mgc**, **nia**, **ocu**, **rht**, **she**, **soc**, **spn**, **tbo**, **the**, **toc**, **ttt**, **twf**
10	**lcs**, **lvt**, **lcy**, **srs**	**ith**, **scu**, **shp**, **stp**
12	**lcv**	**alb**, **pto**
14	**qtz**	**pts**
16	**bcs**	**sqc**
20	**thp**	**csq**, **ssa**, **ssb**
24	**ana**	**gar**, **iac**, **ibd**, **pyr**, **ssc**
28		**ifi**
32		**ctn**, **pth**

kinds of tile, each with one kind of face. In this case, then, in order to make the tiling face-transitive, two tiles of the same kind may never share a face.

Similarly to Dress *et al.* (1993), we started by finding all potential tiles with either one kind or two kinds of face but without divalent vertices. From these we construct all possible tiles that correspond to a given target D-symbol size by splitting edges and inserting new nodes of valency 2.

In the next step, we generate candidate Delaney symbols by looking at all possible ways of connecting one or two given kinds of tile from our previous list. Not all of these will correspond to actual tilings of regular space. Finding out which do can be rather difficult. In practice, however, this can usually be decided relatively quickly by using a method described by Delgado-Friedrichs (2001).

Finally, we determine all the nets that these tilings carry, extract the proper ones and remove duplicates (Delgado-Friedrichs & O'Keeffe, 2003); this procedure is implemented as part of the software package *Gavrog* (http://www.gavrog.org) by the first-named author. The number of candidate nets before screening increases rapidly to some thousands, and the computing becomes onerous, as the D-symbol size increases, so we need to cut off the generation process at some point. We determined that all the known edge-transitive nets had proper tilings with a D-symbol size ≤ 32 so this was used as a target. Notice that what we call natural tilings (Delgado Friedrichs *et al.*, 2003*a*,*b*, 2006) are sometimes derived as subdivisions of tilings with the minimum D-symbol size and hence have larger size.

Tiles are topological spheres and in Fig. 1 we show some illustrative examples as tilings of the surface of a sphere. The first row shows a tetrahedron [3^4] (left) converted to a tetrahedron [6^4] (adamantane unit) by inserting six extra vertices. On the right in the figure is shown the adamantane unit as it

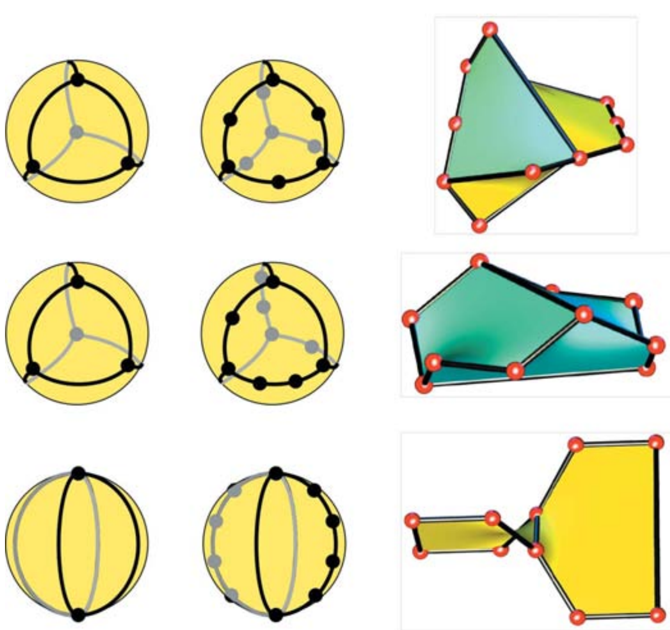

Figure 1
Left: from top tilings [3^4], [3^4] and [2^4] of the surface of a sphere. Middle: derived [6^4] tilings. Right: embeddings of these tiles in tilings discussed in the text.

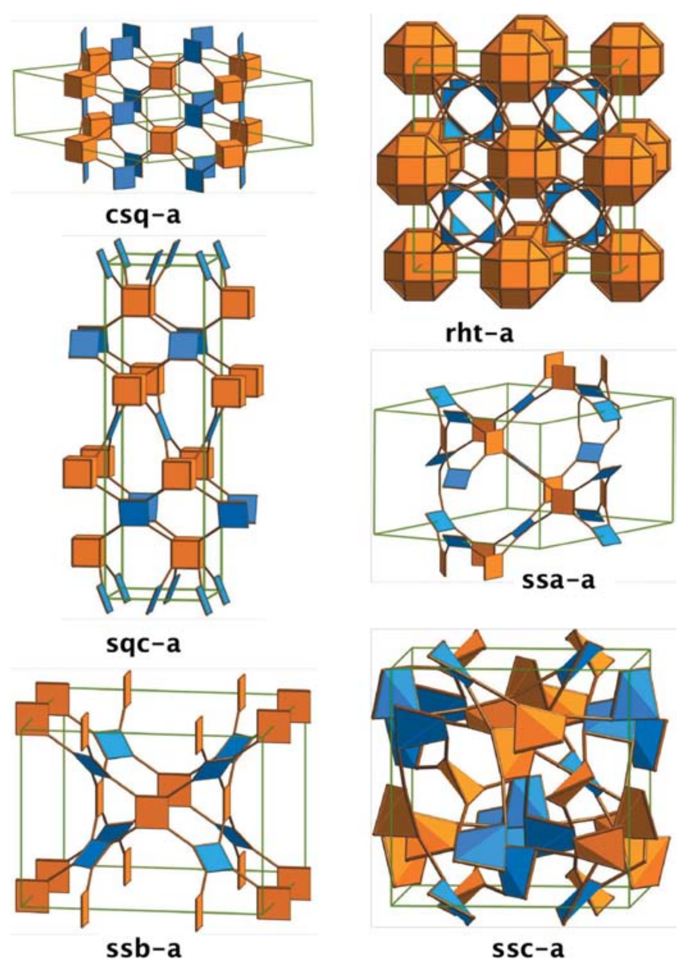

Figure 2
Augmented versions of the new edge-transitive nets found in this paper.

Table 2
Edge-transitive nets with two vertices of coordination number Z.

'symb' is the symbol for the net, 'ps' refers to point symmetry of order o'. 'sg' refers to space group and 'trans' to transitivity of the tiling. Each of the two lines for each net provide data for one of the two vertices.

Z	Vertex figure	symb	ps	o'	sg	x, y, z	Tiles	trans
3, 24	Triangle	**rht**	$3m$	6	$Fm\bar{3}m$	0.3333, x, x	$6[4^4]+2[4^6]+[4^{12}]$	2123
	Rhombicuboctah.		$m\bar{3}m$	48		0, 0, 0		
4, 4	Quadrangle	**ssa**	$2/m$	4	$P6_3/mmc$	0, 1/2, 0	$[4^3.6^2]+[4^3.6^2.8^3]$	2143
	Quadrangle		$mm2$	4	$c/a = 1/\sqrt{2}$	x, $2x$, 1/4	$+[8^3.12^2]$	
4, 4	Quadrangle	**ssb**	$2/m$	4	$I4/mmm$	1/4, 1/4, 1/4	$[4^4.8^2]+[4^4.8^6]$	2143
	Quadrangle		$mm2$	4	$c/a = 1/\sqrt{2}$	0, 0.25, 0	$+2[8^4]$	
4, 4	Quadrangle	**ssc**	222	4	$I4_132$	0, 1/4, 1/8	$[6^2.10^6]$	2131
	Quadrangle		222	4		0, 1/4, 5/8		
4, 8	Quadrangle	**sqc**	$2/m$	4	$I4_1/amd$	0, 1/4, 3/8	$2[4^3.6^2]+[4^2.6^4]$	2121
	Cube		$\bar{4}m2$	8	$c/a = \sqrt{10}$	0, 0, 0		
4, 8	Quadrangle	**csq**	$mm2$	4	$P6/mmm$	0.25, x, 1/2	$4[4^3.6^2]+3[4^4]$	2155
	Cube		mmm	8	$c/a = 1/\sqrt{8}$	0, 1/2, 0	$+2[4^6.12^2]$	

appears in the tiling whose dual carries the edge-transitive net **ana** (this is the net of the zeolite framework with code ANA). In this tiling, the tile has symmetry 2 (C_2) and the faces are of two kinds, shown as yellow and blue in the figure. The second row in the figure shows the generation of a different $[6^4]$ tiling from $[3^4]$. In the third row yet another $[6^4]$ tile is derived – this time starting from $[2^4]$. The second and third tiles combine to form a tiling whose dual carries a new binodal edge-transitive net (**ssc**). Note that in this example the graph of the face-transitive tiling includes 2-rings (multiple edges) and would not be considered as a crystal net. However we are interested only in the graphs of the duals, and this objection does not arise for the dual in this case.

3. Results

61 distinct edge-transitive nets were found for tilings with D-symbol size ≤ 32. Of these, seven did not fit our criteria (had short non-edge intervertex distances). Symbols for the rest are listed in Table 1. Of these, six did not appear in our previous compilations (Delgado Friedrichs *et al.*, 2003*a*,*b*, 2006)[2] – some relevant properties of these are listed in Table 2. These new nets are illustrated in augmented form (vertices replaced by a vertex figure of vertices) in Fig. 2.

Two of the rejected uninodal nets are worth a brief mention. The first is derived from the lattice complex Y (Fischer & Koch, 1983). The net of the structure with nearest-neighbor distances as edges appears in our earlier report (Delgado Friedrichs *et al.*, 2003*b*) with symbol **lcy**. The net with the 12 second-neighbor distances as edges (known to the RCSR database as **lcz**) is one of the rejected structures. The vertices of the lattice complex W have only two neighbors and the graph (**lcw**) of the vertices and edges corresponding to the nearest neighbors consists of disjoint 1-periodic graphs, and hence is not considered a crystal net. However, the graph derived by identifying second-neighbor distances as edges is connected and edge-transitive (and known to RCSR as **lcx**).

[2] **rht** was known but inadvertently omitted from Delgado-Friedrichs *et al.* (2006).

These two examples show that we might expect to derive infinite families of edge-transitive nets by starting from symmetrical arrays and identifying edges as links to increasingly distant neighbors. This is indeed the case, and we have found, in an unpublished study, 25 infinite families of periodic edge-transitive nets with just one vertex in the repeat unit ('lattice nets'). So in a sense the 'whiff of unsatisfactoriness' mentioned in the *Introduction* remains, although we hope it is now less pronounced.

On the positive side, we note that no new vertex- and edge-transitive nets with edges corresponding to shortest distances were found, suggesting that our list may have been complete. This belief is bolstered by a study of Blatov (2007) which enumerated all subnets of known vertex-transitive nets and which found no new edge-transitive structures. We also take pleasure in the observation that all previously known structures were generated in our search; this once again shows the utility of tiling theory in systematically generating nets.

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