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A New Group of Edge-Transitive 3-Periodic Nets and Their Derived Nets for Reticular Chemistry

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ABSTRACT: Edge-transitive and related minimal transitivity nets play a central role in the designed synthesis of crystalline framework materials (reticular chemistry), in particular, metal–organic frameworks (MOFs). We report a new family of thirteen edge-transitive nets that have previously gone unidentified theoretically and their associated minimal transitivity nets. Their relevance to existed materials is noted, uncovering new nets with minimal transitivity 3 2 (three kinds of nodes and two kinds of edges), mostly never known or observed in real crystals, for future design.

INTRODUCTION

Nets with one kind of edge (edge-transitive nets) play a central role in reticular chemistry.[1-3] The number of such nets which have a straight, non-intersecting edge embedding is limited. For example, excluding the 13 new nets reported here, in the Reticular Chemistry Structure Resource (RCSR)[4] only 39 of 747 binodal nets are edge-transitive. We should note though that if intersecting edges are allowed (normally they are not) then there are infinitely many as in the edge-transitive lattice nets.[5]

Associated with edge-transitive nets are their *derived* and *related* nets with minimal transitivity - e.g. three kinds of nodes and two kinds of edges - transitivity 3 2. These are particularly important in the large class of materials like metal–organic frameworks (MOFs) with branched polytopic linkers.[3,6,7,8] The minimal transitivity principle, when applied to the outcome of a reticular synthesis, says one gets a net as simple as possible, that is, with the minimal transitivity compatible with the local structure (e.g. secondary building units, i.e. SBUs, and linkers) and stoichiometry.[3] So far we know all trinodal polyhedra and 2-periodic nets with transitivity 3 2,[9] but those 3-periodic ones have not, as yet, been systematically derived.

In this report we identify a group of binodal edge-transitive nets that, except for two examples, have previously gone unidentified in theoretical enumeration,[2] as well as in RCSR.[3,4] We elaborate here how the new nets arise, why they are important but have largely been unknown, and what derived nets with transitivity 2 2 and 3 2 they give rise to. The occurrences of these nets in real crystals in the ToposPro[10] database are explored, enriching the latest chapter of reticular chemistry.[7]

RESULTS AND DISCUSSION

Identification of New Nets. We start with known edge-transitive binodal nets (the parent net) in which at least one vertex to be split into pairs is in planar coordination. A further requirement is that the symmetry at that vertex is sufficient to allow splitting into a symmetry-related pair and maintain edge transitivity. This results in identification of 13 binodal edge-transitive nets (the daughter net) listed in Table 1 in which the coordination numbers and vertex figures are indicated.

We describe the first example here to illustrate how the parent gives birth to the daughter. The net **srs** is the unique 3-coordinated (3-c) edge-transitive net and has symmetry $I4_132$. In a *binary* version **srs-b** two sets of vertices, say A and B, are distinguished ("colored") and the symmetry is lowered to $P4_332$. If now the B vertices with symmetry 32 are split into pairs of vertices B' with symmetry 3, as shown in Figure 1, a new edge-transitive net **cys** is obtained with A now in 6-coordination and B' in 3-coordination. The net has been identified earlier as the labyrinth net of the $C(Y)$ minimal surface.[11] It has also been found in a computer search for edge-transitive nets.[12]

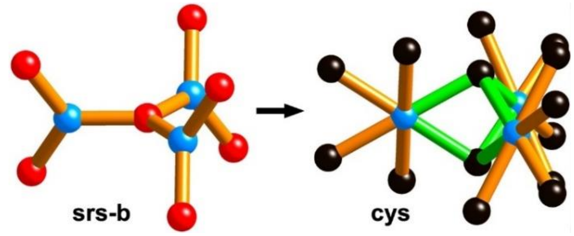

Figure 1. The generation of a binodal edge-transitive net (**cys**) from a uninodal net (**srs**).

Table 1. New Edge-Transitive Nets and Their Parent and Derived 3 2 Nets

Parent	CN[a] (VF[b])	Daughter	CN[a] (VF[b])	Derived 3 2	CN[a] (VF[b])
srs-b	3,3 (3,3)	**cys**	3,6 (3,H)	**pyo**	3,3,3 (3,3,3)
nbo-b	4,4 (S,S)	**cyt**	4,8 (S,E)	**gee**	3,4,4 (3,S,S)
hxg-b	6,6 (H,H)	**cyu**	6,12 (H,D)	**hxh**	3,6,6 (3,H,H)
tbo	3,4 (3,S)	**nts**	4,6 (S,H)	**ntt**	3,3,4 (3,3,S)
pto	3,4 (3,S)	**cya**	3,8 (3,E)	**cza**	3,3,4 (3,3,S)
		cyb	4,6 (S,H)	**czb**	3,3,4 (3,3,S)
pts	4,4 (S,T)	**cyc**	4,8 (S,C)	**csc**	3,4,4 (3,S,T)
she	4,6 (S,H)	**cyd**	4,12 (S,D)	**czd**	3,4,6 (3,S,H)
		cye	6,8 (H,E)	**cze**	3,4,6 (3,S,H)
stp	4,6 (S,P)	**dfs**	4,12 (S,X)	**ood**	3,4,6 (3,S,P)
				dfv	3,4,5 (3,S,Q)
scu	4,8 (S,C)	**cyg**	4,16 (S,G)	**cxg**	3,4,8 (3,S,C)
				czg	4,4,5 (S,S,Q)
shp	4,12 (S,X)	**hfz**	4,24 (S,M)	**hfx**	3,4,12 (3,S,X)
				hfy	4,5,6 (S,Q,H)
ftw	4,12 (S,B)	**cyf**	4,24 (S,W)	**xba**	4,4,8 (S,T,C)

[a] CN = coordination number. [b] VF = vertex figure, for which 3 = triangle, S = square, T = tetrahedron, Q = square pyramid, P = trigonal prism, H = hexagon, C = cube, E = octagon, B = cuboctahedron, X = hexagonal prism, D = dodecagon, G = octagonal prism, M = dodecagonal prism, W = truncated cube.

An important feature of the net is that pairs of *B*' vertices have the same neighbors (Figure 1, right). This means that the automorphisms of the graph include the operation of interchanging the vertices of such pairs keeping the rest unchanged. This operation is known as a *local* symmetry or a *nonrigid body* symmetry. On the other hand crystallographic symmetry operations act globally - they are *rigid body* symmetries. Accordingly a net such as **cys** is considered *non-crystallographic* (NC) and is rejected by the program Systre which identifies nets and their symmetries.[13] This is the reason why the present family of edge-transitive nets were largely overlooked[1-3] and absent in RCSR. An important observation is however that the *augmented* net, in which vertices are replaced by their coordination figures, and the derived nets, are mostly *crystallographic*.

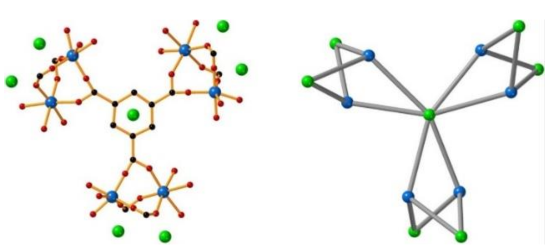

Figure 2. Left: a fragment of a Zn MOF (Zn blue) with a tritopic linker centered with a green ball. Right: a fragment of the net obtained by linking the green nodes with Zn nodes.

Interestingly, the **cys** net can be recognized in the structure of an early MOF, zinc trimesate.[14] In the *standard representation* of the ToposPro program[10] the underlying net of a simple MOF with one metal-containing SBU and one polytopic linker is found by connecting metal atoms as nodes to nodes at the centers of the linker.[15,16] As shown in Figure 2 the net is **cys** for the MOF in question.

A second NC edge-transitive net, (4,6)-c **nts**, has also been recognized. This is because its derived 3 2 net, **ntt**, is the underlying net of a large group of MOFs, which had ultrahigh surface area and were described in several ways (e.g. **rht**-MOFs).[3,8,17,18] It went unrecognized in earlier enumeration[19] of edge-transitive nets because of its NC nature.[20] The only other edge-transitive net with square and hexagon (VF = S,H) is the crystallographic net **she**.[3]

After the present work was started a third NC edge-transitive net, (4,12)-c **dfs**, was identified in a MOF with its derived net (transitivity 2 2).[21] Previously the only edge-transitive net offered for joining square and hexagonal prism (VF = S,X) is (4,12)-c **shp**,[19] with extensive theoretical enumeration of nets and experimental design of real MOFs achieved.[7] The **dfs-a** (augmented version) net, with even larger voids compared with **shp-a**, represents an unexplored platform for designed synthesis.

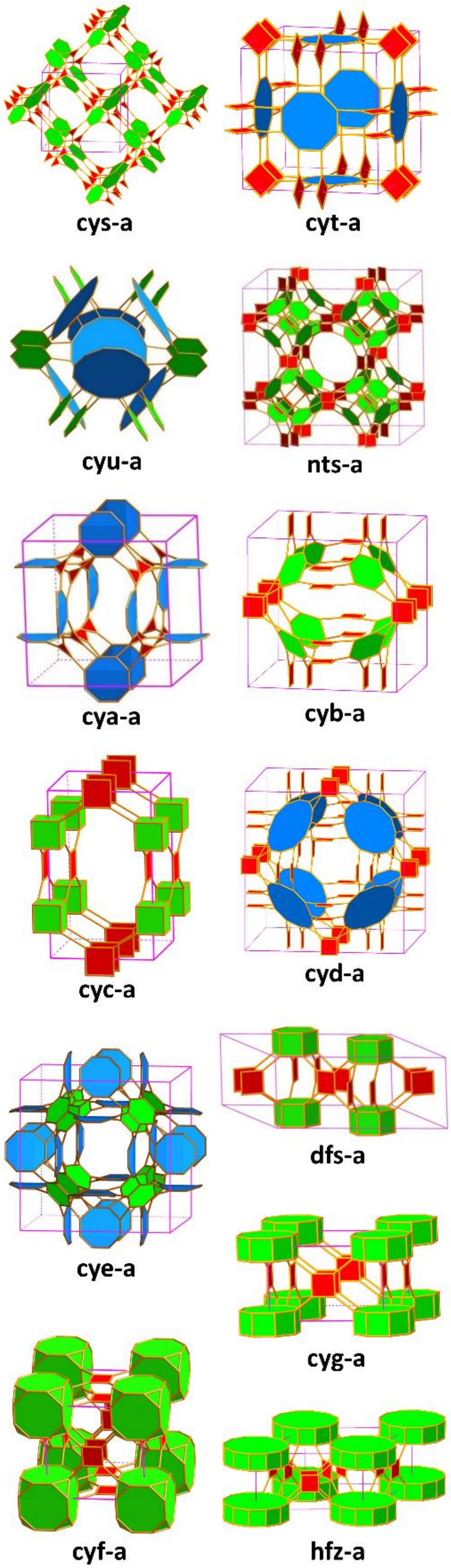

Figure 3. Augmented versions of the new edge-transitive nets.

The 13 new edge-transitive nets are illustrated in augmented form in Figure 3. Note that all the nets are deposited in RCSR and can be searched by their vertex figures (e.g. **nts** is a SH net; search "SH net" in "names" option in RCSR).

Derived Nets. The process of obtaining derived nets has been described in detail elsewhere.[3,7] Briefly one vertex of the original net is replaced either by a pair of linked vertices to produce a new net with transitivity 2 2 or by a group of vertices to produce a new net with transitivity 3 2.

Many of these new edge-transitive nets have planar 4-c vertices. These vertices can be split into two 3-c vertices to produce a derived 2 2 net. However, particularly when the other vertices are also in planar coordination, e.g. hexagon (H), octagon (E) and dodecagon (D), this results in structure in which vertices not directly linked come close together. We only consider the derived 2 2 nets from those having a non-planar vertex figure - that is, **cyc** (SC net), **dfs** (SX net), **cyg** (SG net), **hfz** (SM net) and **cyf** (SW net) - as suitable targets for reticular chemistry. The derived 2 2 nets are illustrated in the Supporting Information (Table S1 and Figure S1–S5).

More interesting are the derived 3 2 nets. The 3 2 nets derived from or related to crystallographic edge-transitive nets are topical in current reticular chemistry as the underlying nets of truly designable MOF materials (e.g. **shp**-, **alb**- and **soc**-MOF platforms).[7,22,23] Those derived from NC edge-transitive nets remain unexplored for targeted synthesis, especially for those with highly-connected, non-planar vertex figures, e.g. hexagonal prism (X, CN = 12), octagonal prism (G, CN = 16), dodecagonal prism (M, CN = 24) and truncated cube (U, CN = 24).

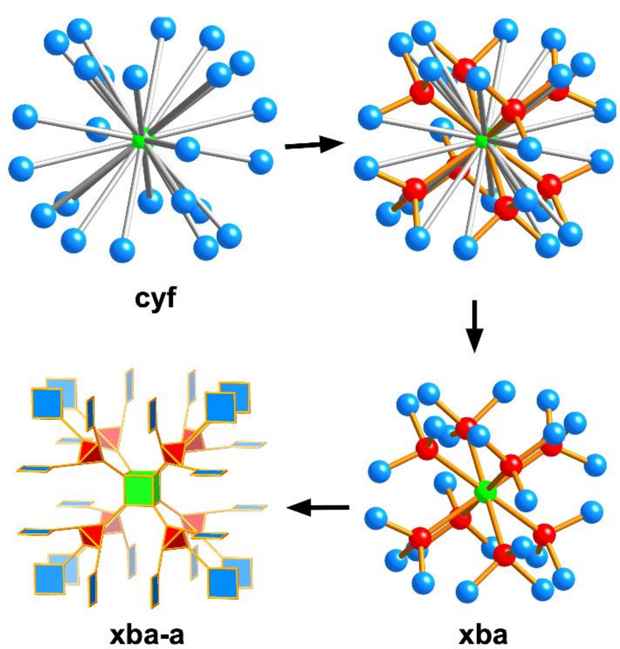

Figure 4. Top left: the 24-c vertex (green) of (4,24)-c **cyf** net, transitivity 2 1. The blue vertices form a truncated cube. Top right: inserting eight new vertices (red) 8-coordinated to the central green vertex so that the red vertices are in tetrahedra (one green and three blue vertices). Bottom right: deleting the original edges gives a derived net, **xba**, with transitivity 3 2. Bottom left: the augmented version of the derived net.

We describe the last example in Table 1 to illustrate how to obtain a derived 3 2 net. The new (4,24)-c **cyf** net has the vertex figures of square and truncated cube; the previously known edge-transitive (4,24)-c net, **twf**, has tetrahedron and truncated octahedron.[2] The derived 3 2 net is obtained by replacing the 24-c node with a group of nodes (one 8-c node linked to eight 4-c nodes) while keeping the coordination number of the square nodes unchanged. This can be done in a two-step process shown in Figure 4. The derived net, **xba**, contains the vertex figures of square, tetrahedron and cube, and has the same cubic symmetry ($Pm\overline{3}m$) as **cyf**.

14 of the 16 derived nets with transitivity 3 2 obtained in this work are shown in Figure 5. These are good targets for reticular chemistry. It might be noted that **cyc**-derived **csc** is not included as it is a NC net (shown in Figure S6). Also not included is **nts**-derived **ntt** which is well documented.[3,20] The full unit cell for **hxh** is shown in Figure S7.

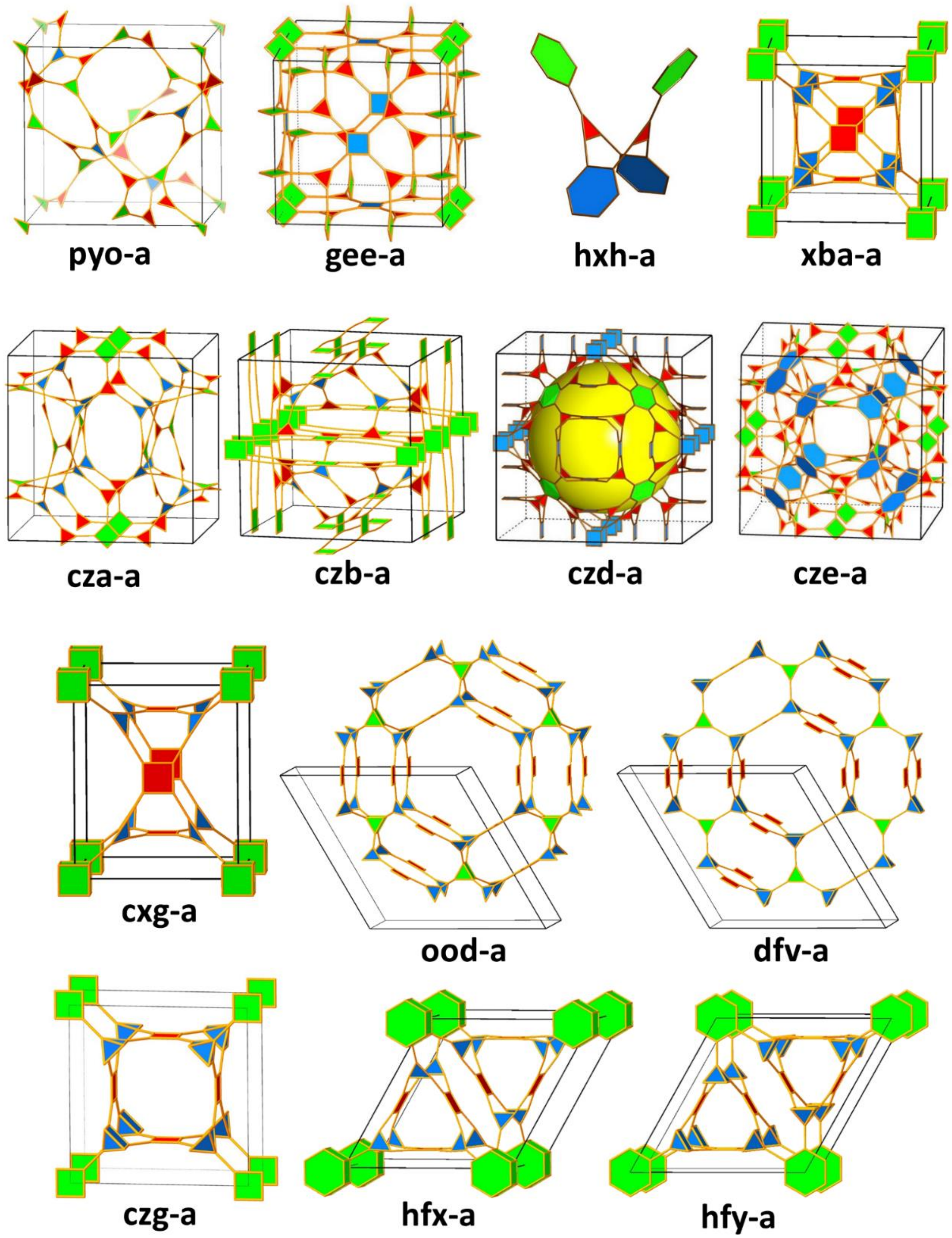

Figure 5. Augmented versions of the derived nets with minimal transitivity 3 2.

Table 2. Occurrences and Names of NC Edge-Transitive Nets and Their Derived 3 2 Nets

Occurrences [a] standard representation	Occurrences [a] cluster representation	RCSR name	SPGR [b]	ToposPro name(s)
	EDGE TRANSITIVE NETS - NC - transitivity 2 1			
19	9 (6 single, three 2-fold)	**cys**	$P4_332$	**cys**
161	-	**cyt**	$Pm\overline{3}m$	4,8T24
-	-	**cyu**	$Fd\overline{3}m$	NEW
106	3 (disorder) [c]	**nts**	$Fm\overline{3}m$	**nts**; 4,6T4
-	-	**cya**	$Pm\overline{3}n$	NEW
32	-	**cyb**	$Pm\overline{3}n$	4,6T119
28	3 (2-fold, TBU cluster) [d]	**cyc**	$P42/mmc$	**alb**-4,8-P42/mmc
3	-	**cyd**	$Im\overline{3}m$	4,12T65
-	-	**cye**	$Im\overline{3}m$	NEW
1	-	**dfs**	$P6/mmm$	4,12T9
36	-	**cyg**	$P4/mmm$	4,16T2
10	-	**hfz**	$P6/mmm$	4,24T1
-	1 (disorder) [c]	**cyf**	$Pm\overline{3}m$	4,24T3
	DERIVED NETS - transitivity 3 2			
-	-	**pyo**	$P4_132$	**pyo**; 3,3,3T3
-	1 [e]	**gee**	$Pm\overline{3}m$	**gee**
-	-	**hxh**	$Fd\overline{3}m$	NEW
-	55	**ntt**	$Fm\overline{3}m$	**ntt**
-	-	**cza**	$Pm\overline{3}n$	NEW
-	-	**czb**	$Pm\overline{3}n$	NEW
-	-	**csc**	$P42/mmc$	NEW (NC)
-	-	**czd**	$Im\overline{3}m$	NEW
-	-	**cze**	$Im\overline{3}m$	NEW
-	-	**ood**	$P6/mmm$	**ood**
-	-	**dfv**	$P6/mmm$	NEW
-	-	**cxg**	$Pm\overline{3}m$	NEW
-	-	**czg**	$P4/mmm$	NEW
-	-	**hfx**	$P6/mmm$	NEW
-	-	**hfy**	$P6/mmm$	NEW
-	-	**xba**	$Pm\overline{3}m$	**xba**

[a] In topcryst.com (Jan 2020). [b] SPGR = space group. [c] These findings are an artifact of the automatic classification due to the presence of structures in which one ligand is disorder on two positions. [d] CCDC refcodes: EFESEP, EFESIT, EFESOZ (isomorphous). [e] CCDC refcode: KOZQEX.

Occurrences. The standard representation of ToposPro[10,15] finds examples for 9 of 13 of this new family of edge-transitive nets, deposited in the Samara Topological Data Center, https://topcryst.com/ and accessed by searching with the appropriate names (see Table 2 for the correspondences with RCSR names).

The most frequent underlying net is (4,8)-c **cyt** (known to ToposPro as 4,8T24) observed in 161 MOFs. As previously described in Table 1 of reference 15 it is the standard representation of the net of MOFs with square paddlewheel SBUs linked by tetratopic linkers that in the "all node" or "single node" *cluster representation* have the nets **fof**, **fog**, **tfb**, or **nbo**, which have been designed extensively in MOF field.[3] In the cluster representation which can identify the components of metal SBUs and organic linkers,[15] a few interesting examples are isolated: (4,8)-c **cyc** (and its derived 2 2 net (3,8)-c **cwc**) are identified for three isomorphous two-fold interpenetrated MOFs (Figure 6, see also Table S2) reported in 2014;[24] (3,6)-c **cys** is observed in 9 structures (3 of which 2-fold interpenetrated) all presenting the same ligand pattern[14] (two almost eclipsed trisubstituted 6-rings, see Figure S8).

14 of the 16 derived nets with transitivity 3 2 were never known or observed in MOFs (see Table 2), except for the frequently studied MOFs with **ntt** net (aka. **rht**-MOFs)[3] found in 55 examples and two isoreticular mesoporous MOFs with **gee** net.[25]

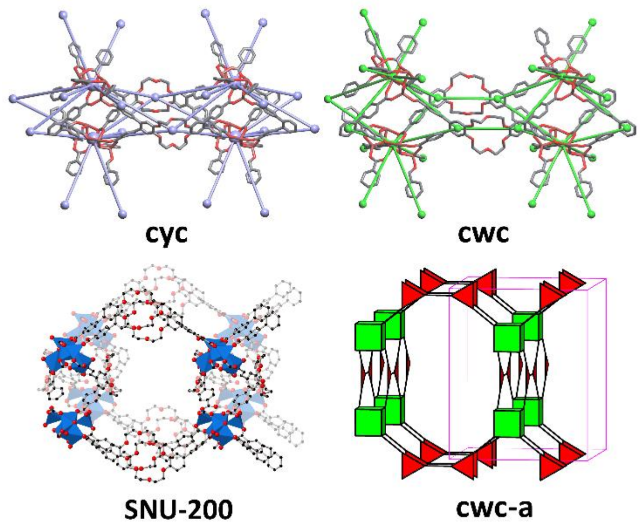

Figure 6. The underlying net of SNU-200. Top left: ToposPro "single node" (TBU) cluster representation giving (4,8)-c **cyc**. Top right: "all node" cluster representation giving derived net (3,8)-c **cwc**. Bottom left: a fragment of the MOF structure (Zn: blue polyhedra). Bottom right: augmented net **cwc-a**.

Design Scheme. (i) *Predesign*. The first step to design a MOF with a NC edge-transitive net is to choose a suitable underlying net. Among the 13 new edge-transitive nets, the ones containing non-planar vertex figures, i.e. **cyc**, **dfs**, **cyg**, **hfz** and **cyf**, are selected because metal SBUs or organic linkers forming highly-coordinated planar polygons (CN ≥ 8) are rare. A second consideration is two 4-c squares in these nets are very close (see Figure 3) so that it might be unattainable in real MOFs, and thus the derived 2 2 nets are used for introducing branched tetratopic linkers with two 3-c nodes (see Table S1–S2 and Figure S1–S5).

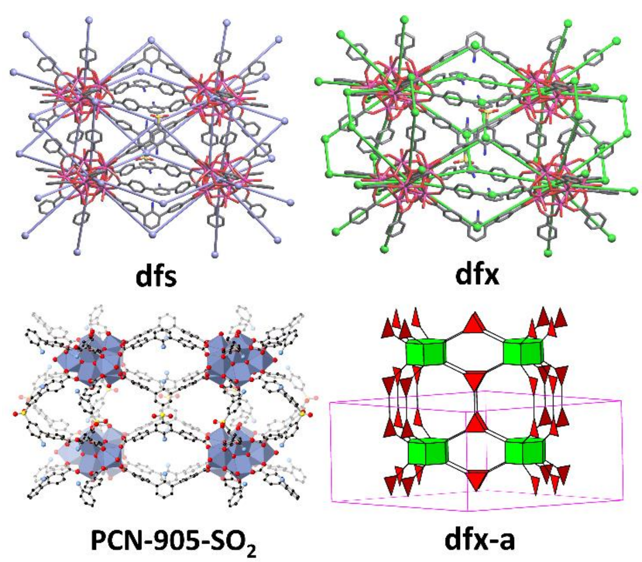

Figure 7. The underlying net of PCN-905-SO$_2$. Top left: ToposPro "single node" (TBU) cluster representation giving (4,12)-c **dfs**. Top right: "all node" cluster representation giving derived net (3,12)-c **dfx**. Bottom left: a fragment of the MOF structure (Eu: purple polyhedra). Bottom right: augmented net **dfx-a**.

The recently reported PCN-905-SO$_2$[21] contains a bent branched tetracarboxylate linker which can ease the crowding of adjacent ligands in the resulting MOF with a **dfs**-derived net (Figure 7). Note that there are two ways of obtaining the derived 2 2 nets (**dfx** and **dfw** in Figure S2) so the underlying net is **dfs**-derived **dfx** explicitly. A similar strategy of using semirigid linkers can be proposed from above mentioned SNU-200[24] with **cyc**-derived **cwc** net (Figure 6, see also Figure S1).

The challenge is to establish the chemistry for predictable synthesis of the metal SBUs forming the highly-coordinated polyhedra for these NC edge-transitive nets. As one might notice the $Zn_5(OH)_2(-CO_2)_8$ SBU in SNU-200[24] and $RE_9O_2(OH)_{12}(-CO_2)_{12}$ SBU in PCN-905-SO$_2$[21] are not the common SBUs documented, further studies are encouraged.

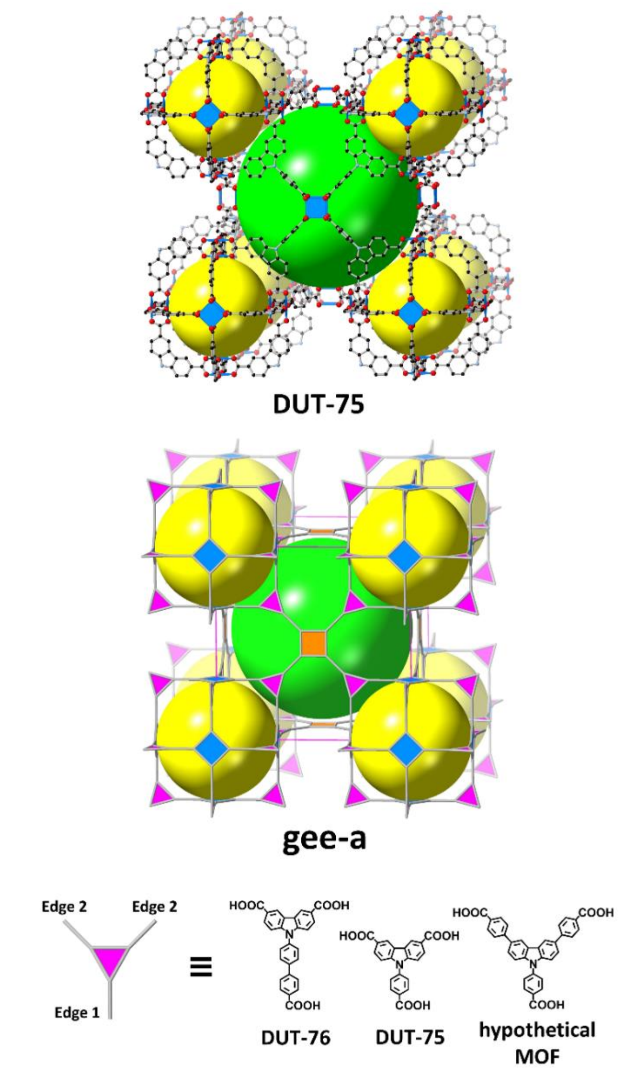

Figure 8. The underlying augmented net, **gee-a**, of DUT-75 (Cu: blue squares) and post-design on the tritopic linker by taking advantage of the minimal transitivity 3 2.

(ii) *Post-Design*. The *de novo* synthesis of MOFs with the derived 3 2 nets is difficult because, unlike the limited options for connecting two types of regular figures in an edge-transitive net, the possibilities for three are still unclear.[9] Hence the design of this sort usually starts from recognition of tertiary building unit (TBU)[3,7] or supermolecular building block (SBB),[17] e.g. a highly-connected metal–organic polyhedron, in a certain MOF. The opportunities offered for design in an underlying net with minimal transitivity 3 2 include the two types of edges within a linker can be varied independently in isoreticular expansion. For example, similar to the well-studied MOFs with **ntt-a** net (see Figure 56 of reference 3), the two segments of the tritopic ligand, when linked to the common $Cu_2(–CO_2)_8$ paddle wheel SBU, in DUT-75[25] with **gee-a** net can be modified separately to tune the relative size of two cages (large yellow and green balls in Figure 8) as one wishes. A hypothetical MOF is proposed here for tuning the size of the yellow ball instead of the green one as done in DUT-76.

Another interesting platform for similar design is **dfs**-derived **ood** net (see Table 1 and Figure 5 **ood-a**), which contains triangle, square and trigonal prism, all common regular figures in reticular chemistry. The **dfs**-derived 2 2 net **dfx** was recently observed;[21] realization of a new MOF with **dfs**-derived 3 2 net **ood** which features extra-large voids is a prerequisite for post-design. The rest in Figure 5 will be given over to future design in the latest chapter of *Reticular Chemistry 3.2*.[7]

CONCLUSIONS

Since the advent of reticular chemistry theoretical prediction of underlying nets has been guiding the designed synthesis of MOFs and other crystalline porous materials. Over the course of development it turns out experiments can also complement theory—the identification of this new group of 13 edge-transitive nets is a best exemplification. The alliance of RCSR and TopoSPro databases uncovers their derived nets with three kinds of nodes and two kinds of edges (minimal transitivity 3 2), 14 of 16 never known or observed, for future design, a new adventure already begun most recently.

EXPERIMENTAL SECTION

Methods and Data. All of the nets were conceived and constructed manually using the commercial software CrystalMaker X. For crystallographic nets symmetry computation were performed using the program Systre[13] which rejects identification of non-crystallographic nets. All the nets, including the NC ones, were analyzed with the program ToposPro[10] and the occurrences in crystalline materials were checked in the regularly updated Samara Topological Data Center (access at https://topcryst.com/). The supplemented .cgd files which specify the nets are readable by Systre and ToposPro. In concurrence with preparation of this paper, all the nets were put in and can be accessed at the searchable database Reticular Chemistry Structure Resource (RCSR, access at http://rcsr.net/).[4]

ASSOCIATED CONTENT

Supporting Information. The following files are available free of charge.

Supplementary Table S1–S2 and Figure S1–S8 (PDF)

Systre net files of new edge-transitive nets and their derived 2 2 and 3 2 nets (CGD)

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Notes

The authors declare no competing financial interest.

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For Table of Contents Use Only

Title: A New Group of Edge-Transitive 3-Periodic Nets and Their Derived Nets for Reticular Chemistry

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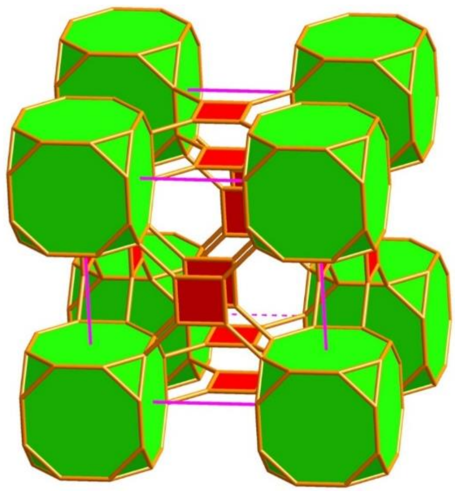

Synopsis: Edge-transitive net is a core concept in reticular chemistry; previously only 39 of this sort containing 2 kinds of nodes and 1 kind of edge (i.e. transitivity 2 1) are known to the Reticular Chemistry Structure Resource (RCSR). In this work a new family of 13 edge-transitive nets are reported (one of them shown in picture), along with their derived nets with minimal transitivity 3 2.