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ARTICLE

Minimal Edge-Transitive Nets for the Design and Construction of Metal-Organic Frameworks

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 Received 00th January 20xx,
 Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Highly-connected and minimal edge-transitive nets (with one or two kinds of edge) can be regarded as ideal blueprints for the rational design and construction of metal-organic frameworks (MOFs). Here we report and affirm the prominence of highly-connected nets as suitable targets in reticular chemistry for the design and synthesis of MOFs. Of special interest are augmented highly-connected binodal edge-transitive nets embedding a unique and precise positioning and connectivity of the net vertex figures, regarded as net-coded building units (**net**-cBUs). Explicitly, a definite **net**-cBU encompasses precise geometrical information that codes uniquely and matchlessly a selected net, a compelling perquisite for the rational design of MOFs. Interestingly, the double six-membered ring (d6R) building unit offers great prospective to be deployed as a **net**-cBU for the deliberate reticulation of the sole two edge-transitive nets with a vertex figure as a d6R, namely the (4,12)-coordinated **shp** net (square and hexagonal prism) and the (6,12)-coordinated **alb** net (aluminium diboride, hexagonal prism and trigonal prism). Conceivably, we envisioned and proposed various MOF structures based on the *derived shp* and *alb* nets. Gaining access to the requisite **net**-cBUs is essential for the successful practice of reticular chemistry; correspondingly organic and organic chemistries were deployed to afford concomitant molecular building blocks (MBBs) with the looked-for shape and connectivity. Practically, the combination of the 12-connected (12-c) rare-earth (RE) polynuclear, points of extension matching the 12 vertices of the hexagonal prism (d6R) with a 4-connected tetracarboxylate ligand or a 6-connected hexacarboxylate ligand afforded the targeted **shp**-MOF or **alb**-MOF, respectively. Intuitively, a dodecacarboxylate ligand can be conceived and purported as a compatible 12-c MBB, plausibly affording the positioning of the carbon centers of the twelve carboxylate groups on the vertices of the desired hexagonal prism building unit, and combined with the complementary 4-c copper paddlewheel [Cu₂(O₂C-) ₄] cluster or 6-c metal trinuclear [M₃O(O₂C-) ₆] clusters/ zinc tetranuclear [Zn₄O(O₂C-) ₆] clusters to credibly afford the construction of new MOF structures with underlying topologies based on *derived shp* and *alb* nets.

Introduction

Metal-organic frameworks (MOFs), an emerging class of hybrid solid-state materials, are recognized to offer prospective properties appropriate for various key application including gas storage/separation¹⁻⁵ and catalysis⁶⁻⁹, due to their unique attributes (e.g. crystallinity, synthesis under mild reaction conditions and structure/composition diversity).¹⁰ Notably, the ability to design and deliberately construct functional MOFs offers great potential to address various enduring challenges pertaining to global energy security and environmental sustainability. Prominently, the practice of reticular chemistry and the molecular building block (MBB) approach permit the rational construction of functional MOFs with the looked-for functionality and properties preprogrammed in preselected MBBs at the design stage, before the assembly process.^{3, 11-15} In this regard, the organic/inorganic building blocks were elected to comprise the desired directional and structural information, akin to the

requisite **net**-coded building units (**net**-cBUs) that code distinctively and matchlessly a selected net.^{14, 16}

Certainly, edge-transitive nets (transitivity [21] or [11]; one kind of edge) are regarded as suitable targets in crystal chemistry.¹⁷ The successful practice of reticular chemistry dictates: i) the ability to readily access the looked-for MBB with the requisite shape and connectivity; and ii) the structure resulting from their prospective assembly to be exclusive, reticulating a specific targeted net that is particular for the associated building units.^{16, 18, 19} Conceivably, we remarked that highly-connected building units can be reticulated into a limited number of edge-transitive nets.^{13, 20-22} Perceptibly, highly-connected edge-transitive nets, with at least one node

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higher than 8-connected (8-c) or equal to 12-connected (12-c), are of special interest and ideal blueprints in MOF crystal chemistry.^{13, 16, 23} Practically, we recently introduced the 12-c hexagonal prismatic (d6R) MBBs for the design and construction of MOFs based on two unique

Two edge transitive nets based on d6R

Fig.1 Net augmentation of shp and alb net.

highly-connected edge-transitive nets, namely the (4,12)-coordinated **shp** net (square and hexagonal prism) and the

(6,12)-coordinated **alb** net (aluminium diboride, hexagonal prism and trigonal prism).^{16, 24} Specifically, polynuclear

clusters or branched polycarboxylate ligands were successfully employed as the requisite 12-c MBB, reasonably affording the positioning of the carbon centers of the twelve carboxylate groups on the vertices of the desired hexagonal prism (d6R) building unit.

Here we report and introduce the concept of combining **net**-coded building units (**net**-cBUs) and minimal edge-transitive nets as a powerful strategy for the design and construction of MOFs. As a case study and proof of concept, the sole two highly connected edge-transitive nets with a double six-membered ring (d6R) building unit, namely the **shp** net and the **alb** net, were carefully chosen to derive novel minimal edge-transitive nets. In both **shp** and **alb** cases, the *derived* nets showed minimal transitivity (the simplest possible) and all links (edges of the net) are equivalent by symmetry. Minimal edge-transitive **shp**-*derived* nets and **alb**-*derived* nets (transitivity [32]) were enumerated and associated plausible MOF structures were proposed/simulated based on the attainment of the **net**-cBUs of the parent **shp** and **alb** net as tertiary building units (TBUs).²⁵ That is, for example the hexagonal prism (d6R) as a TBU can be derived from one hexagon building unit linked to six triangles (one kind of triangular building units). Affirmatively, our recently reported new MOF structures attest to the successful implementation of this approach; namely i) Cu-**shp**-MOF-1 was based on a *derived shp* net with the new **cez** underlying topology, and ii) RE-**alb**-MOF-1 and In-**alb**-MOF-1 were based on *derived alb* nets with the **ury** and the **kez** underlying topology respectively. Intuitively, it is suggested that the d6R as a **net**-cBU for the augmented **shp** and **alb** nets can be employed to introduce new TBUs; prompting the simulation/modelling and the subsequent targeting/construction of new MOFs based on other *derived shp* and **alb** nets as appropriate blueprint nets. Prominently, we propose a toolbox for the design and construction of MOFs based on minimal edge-transitive nets.

Results and discussion

Generally, it is more informative to illustrate nets in their augmented versions instead of the original net.²⁶ A net augmentation²⁶ is a process that an n-connected node for a given net is replaced by an associated polygon or polyhedron (vertex figure) with n vertices, leading to an augmented net (net-a). A subsequent vertex figure dictates the essential n points of extension (connectivity), structural and geometrical information to be attained and expressed in the targeted organic/inorganic building block prior to the assembly process into a targeted net. Here, the net augmentation of the two edge transitive nets (namely, 4,12-connected **shp** net (transitivity [2133]) and 6,12-connected **alb** net (transitivity [2134])) results in the related augmented nets, **shp**-a net and **alb**-a net, respectively (Fig. 1). The net augmentation provides the vertex figure associated to net node(s), providing the requisite structural and geometrical information of the relevant secondary building unit (SBU) and to be implemented in the associated particular organic/inorganic chemical entity (MMB). Rationally, further transposition/deconstruction of a

net vertex figure (resultant polygon or polyhedron SBU) affords the introduction of additional point of extension and the generation of the respective TBU, leading to a related derived nets.²⁷ For clarity, all topologies discussed in this contribution are represented as augmented nets.

It is to be stated that **shp**-a and **alb**-a nets are the only binodal edge-transitive nets embedding the hexagonal prim (d6R) vertex figure. Reasonably, the d6R can be regarded as the **net**-cBU for the **shp** and **alb** nets and attainment of such a building units in associated MBBs will facilitate, depending on the connectivity and geometry of the second MBB, the construction of related **shp**- or **alb**-MOFs. Plausibly, employment of branched MBBs offers the prospective to deploy TBUs (embedding two independent SBUs) as the requisite **net**-cBUs. Certainly, a minimal edge-transitive net derived from a specific binodal edge-transitive net, derived by replacing one node by a binodal group and altering the net transitivity form to [32] from the original [21], can be exclusive for the assembly of its corresponding **net**-cBUs. Importantly, the peripheral points of extension of the essential **net**-cBUs (points at which the building units are linked together to generate a net) should match the vertices of the corresponding vertex figures in the targeted net.

The parent net and derived nets

Noticeably, two MOFs with intricate (complicated) linkers with more than 2 branch points can be related to the same parent net but can express different derived nets. Evidently in order to avoid this confusion going forward, it is suggested to list both the associated basic net and the *derived* net with a clear mention of the employed procedure for the deconstruction of the intricate linker. In the *derived* net, each branch point of the linker can be regarded explicitly as a vertex of the underlying net.²⁷ It is our proposition, for design proposes, that the parent net provides the needed directional information to be embedded in the elect MBBs for the design and construction of MOFs while the *derived* net shows the underlying topology with minimal transitivity for the MOFs with the poly-topic linkers.

The relationship between the parent net and the *derived* nets was illustrated in the case of the **shp** and the **alb** nets and their associated *derived* nets. **shp** and **alb** nets are edge-transitive nets with transitivity [21]. As showed in the Table 1 and Fig. 2a, the *derived* nets with transitivity [32] were obtained by replacing the 12-connected vertex (d6R or hexagonal prism) by a binodal group.¹⁶ Notably, in some instances two possibilities are conceivable— one having a doubled c; and replacing the 12-c vertex by one of these conformations gives a *derived* net (Table 1).

Table 1 lists all possible *derived shp* and **alb** nets based on only replacing the 12-c vertex by a binodal group. It is to be noted, that the assigned capital letters are symbols for a given node associated coordination figure (CF), as listed in the reticular chemistry Structure Resource (RCSR): 3 = triangle, S = square, T = tetrahedron, Q = square pyramid, O = octahedron, P = trigonal prism, H = hexagon, X = hexagonal prism. The *derived*

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DOI: 10.1039/C7FD00119C

net connectivity is illustrated by $[X_mY]Z_n$, indicating that Y is linked to m X and n Z. The star indicates the corresponding nodes of *derived* net come from the morphing of the nodes of the parent net.

It is to be stated that other **shp**- and **alb**-derived nets were obtained by replacing the 4-c or 6-c vertex by a binodal group; namely: i) two **shp**-derived nets, the **cec** and **ced** nets, are derived by splitting one 4-c vertex into two 3-c vertices; and ii) two **alb**-derived nets, the **ury** net and **cen** net, are derived by splitting the trigonal prismatic 6-c vertex into four 3-c triangular nodes or two 4-c tetrahedral vertices respectively (Table 2, Fig. 2b and 2c).

Fig. 2 (a) The deconstruction of the 12-c hexagonal prismatic node into two kinds of nodes; (b) the deconstruction of 4-c square node; (c) the deconstruction of 6-c trigonal prismatic node.

Table 1. Derived nets by replacing the 12-c vertex by a binodal group.

operation ^a	symmetry	shp derived	shp CF ^b	alb derived	alb CF ^b
X-1-3	$P\bar{6}m2$	cei	$S_4[Q3]$	ala	$P_4[Q3]$
X-1-3 2c	$P6_3/mmc$	cek	$S_4[Q3]$		
X-1-3 2c	$P6_3/mcm$			ceo	$O^*_4[Q3]$
X-1-6a	$P6/mmm$	cee	$S_2[3H]$	kew	$P_2[3H]$
X-1-6b	$P622$	ceh	$T^*_2[3H]$	key	$O^*_2[3H]$
X-1-6b 2c	$P6/mcc$	cez	$S_2[3H]$	kez	$P_2[3H]$
X-1-6c	$P\bar{3}m1$	ceg	$S_2[3O]$	cep	$O^*_2[3O]$
X-1-6c 2c	$P6_3/mmc$	cej	$S_2[3O]$		
X-1-6c 2c	$P6_3/mcm$			cer	$O^*_2[3P]$
X-1-6d	$P\bar{6}m2$	cef	$S_2[3P]$	ceq	$P_2[3P]$
X-1-6d 2c	$P6_3/mmc$	agw	$S_2[3P]$		
X-1-6d 2c	$P6_3/mcm$			cet	$P_2[3O]$
X-3-6	$P\bar{6}2m$			ces	$P_2[SS_2]$
X-3-6 2c	$P6_3/mcm$	cev	$S_2[SS_2]$	ceu	$O^*_2[SS_2]$

^a X- n_1 - n_2 , X represent overall shape of the building block as hexagonal prism; n_1 represents the number of nodes in the center of this hexagonal prism and n_2 represents the number of derived nodes between the central nodes and vertices; ^b $[X_mY]Z_n$ represents that Y is linked to m X and n Z (Fig. 2a), $[X_mY]$ is derived from the parent net; for coordination figure (CF), 3 = triangle, S = square, T = tetrahedron, Q = square pyramid, O = octahedron, P = trigonal prism, H = hexagon, X = hexagonal prism.

Table 2. Derived nets by replacing the 4-c vertex in the **shp** net or 6-c vertex in the **alb** net by a binodal group.

operation ^a	symmetry	shp derived	shp CF ^b	alb derived	alb CF ^b
S-2a	$P6/mmm$	cec	$[3]X_2$		
S-2b	$P6/mmm$	ced	$[3]X_2$		
P-2	$P6/mmm$			cen	$[T]X_3$
P-1-3	$P6/mmm$			ury	$[33]X_2$

^a In S-x or P-x, S and P represent overall shape of the building block as square and trigonal prism, respectively; and x represents the number of nodes in the center. In P- n_1 - n_2 , n_1 represents the number of nodes in the center of this trigonal prism and n_2 represents the number of derived nodes between the central nodes and vertices. ^b $[X_mY]Z_n$ represents that Y is linked to m X and n Z (Fig. 2c), $[X_mY]$ is derived from the parent net; $[Y]Z_n$ represents that Y is linked to another Y and n Z (Fig. 2b and 2c), $[Y]$ is derived from the parent net; for coordination figure (CF), 3 = triangle, S = square, P = trigonal prism, X = hexagonal prism.

Experimental MOFs based on the alb and alb-derived nets

The rational design and deliberate assembly of the long-awaited (6,12)-c **alb**-MOFs (i.e. RE-**alb**-MOF-1 and In-**alb**-MOF-

1) has been recently reported by our group.¹⁶ The predesigned hexacarboxylate ligand (2,4,6-trimethyl-1,3,5-tri(3,5-di(4-carboxyphenyl-1-yl)phenyl-1-yl)-benzene ($H_6Me-TDCPB$)), provided the requisite trigonal prism and guided the occurrence of the RE hexanuclear carboxylate-based cluster $[RE_6(\mu_3-OH)_8(2-FBzoate)_2(H_2O)_2(O_2C-)_{12}]$, (RE = Y, Tb; 2-fluorobenzoate (2-FBzoate) = $C_7H_4FO_2$) as a 12-c hexagonal prismatic (d6R) MBB, resulting in the formation of the first 3-periodic RE-**alb**-MOF-1. Instinctively, the first Indium-based **alb**-MOF, In-**alb**-MOF-1, was constructed by the successful topological transplantation of the **alb** net. The combination of the trinuclear $[In_3(\mu_3-O)(O_2C-)_6]$ carboxylate-based cluster and a purposely-made dodecacarboxylate ligand, 1,2,3,4,5,6-hexakis[3,5-bis(4-methoxycarbonylphenyl)phenoxymethyl]benzene ($H_{12}HBCPB$), led to the formation of the In-**alb**-MOF-1. Evidently, the carbon centers of the twelve carboxylate groups matched the vertices of the desired hexagonal prism (d6R) building unit.

Markedly, the ligand can alternatively be further deconstructed into two distinct 3-connected nodes in the case of the Y-**alb**-MOF-1. Thus, the topology of the Y-**alb**-MOF-1 can be described as the **ury** topology: a (3,3,12)-connected trinodal net with a minimal transitivity [32]. It is worth to mention that the **ury** net is an **alb**-derived net; namely, **alb** net is the basic net and the **ury** net is the *derived* net from the **alb** net by deconstructing the 6-c nodes into 2 kinds of 3-c nodes (Fig. 3).

Fig.3 Experimental MOFs based on **alb** net and its *derived* net, **ury** net, from a 12-connected RE(III) hexanuclear cluster and a 6-connected organic ligand. RE, C, and O are represented by purple, gray, and red, respectively, and H atoms and solvent molecules are omitted for clarity. RE atoms are represented as polyhedra.

As exemplified in the Fig.4, the dodecacarboxylate ligand in the In-**alb**-MOF-1 can be further deconstructed into one kind of 3-connected nodes and one 6-c node. As a result, the underlying net for this structure is the **kez** net: a (3,6,6)-connected trinodal net with a minimal transitivity [32], a newly **alb**-derived net. It is to be noted that the triangular arms of the 12-c TBU are not perpendicular to the central benzene core, and the dihedral angle between the hexagonal core and each triangle is around 45°, eventually resulting in points of extension of the 12-c TBU (or 12-c HBCPB ligand) to coincide with the vertices of the hexagonal prism (d6R), the 12-c vertex figure of the **alb** net. It is to be mentioned that the linker unit is chiral but the net is not. The overall symmetry of the **kez** net is $P6/mcc$.

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Fig.4 Experimental MOFs based on **alb** net and its *derived* net, **kez** net, from a 6-connected In(III) trinuclear cluster and a 12-connected organic ligand.

Proposed MOFs based on the **alb** and **alb-derived** nets

As depicted in the **Fig.5**, two other **alb-derived** nets, namely **cen** net and **kew** nets, were proposed as targets in order to illustrate the design process of MOF based on minimal edge-transitive nets. The **cen** net was derived from the basic **alb** net through the deconstruction of the trigonal prism **net-cBU** into two symmetrical tetrahedral building units, resulting in a (4,4,12)-connected or (4,12)-connected net (two tetrahedra are equivalent by symmetry). The space group of the **cen** net is *P6/mmm* as the parent **alb** net. The other **alb derived** net, **kew** net derived by deconstructing the d6R **net-cBU** into one type of triangular nodes and one hexagon, is a (3,6,6)-connected net. The dihedral angle in the **kew** net between the triangular arm and the central hexagon is 90°. The **kew** net has the same space group *P6/mmm* as the basic parent net.

Practically in order to specifically target the **cen** net, one of the **alb derived** net, an organic linker can be designed to contain two tetrahedral sub-nodes, presenting the two tetrahedral building units inside the net, then combine it with the RE(III) nonanuclear cluster discovered in our group.^{16, 22} The reported

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Proposed MOFs based on alb net and its derived nets

Fig. 5 Proposed MOFs based on **alb** net and its *derived* nets. RE, In, C, O, and Si are represented by purple, lime, gray, red and light blue, respectively, and H atoms and solvent molecules are omitted for clarity. RE atoms are represented as polyhedral.

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hexacarboxylate ligand 1,4-phenylenebis(tris(4-carboxyphenyl)silane) was carefully chosen from literature²⁸ in combination with RE(III) polynuclear clusters, to propose/simulate the MOF based on the **cen** net. It is to be noted that this organosilicon hexacarboxylate linker has been reported to assemble with Zn₄O building units to form a MOF-5 like cubic framework, with a parent **pcu** net. The overall geometry of the linker is octahedral, with the two embedded tetrahedral sub-units in staggered conformation. In the case of the proposed MOF structure with **cen** net, the overall geometry of the linker is trigonal prism with the two tetrahedra in eclipsed conformation, addressing the plausible **cen**-MOF requirements.

MOFs with **kew** net can be targeted by the combination of the trinuclear metal clusters (e.g. In(III) trinuclear cluster) and a purposely-designed dodecacarboxylate ligand, where the dihedral angle of the arm and the central benzene ring should be about 90°. In the practical design process, the methoxy group in the In-**alb**-MOF-1 (with **alb** derived net, **kez** net) was replaced with the acetylene or *para*-phenylene group in order to introduce rigidity and steric hindrance, plausibly forcing the peripheral arms to be perpendicular to the central benzene ring. Reasonably, it is suggested to plausibly form MOF structures with **kew** net based on these newly designed d6R-shaped ligands in combination with the well documented metal trinuclear clusters. For the purpose of demonstration, the ligand with benzene connection was simulated in combination with the In(III) trinuclear cluster to portray the feasibility of the design strategy and the plausible formation of the targeted MOF with the **alb**-derived **kew** net.

Another example of proposed MOF structures with **alb** derived net is a prospective MOF with the **key** topology. As illustrated in the Fig. 6, the **key** net was derived from the basic **alb** net by deconstructing the hexagonal prism (d6R) into one kind of triangles and one hexagon and by transforming the trigonal prism in the **alb** net into an octahedron. In this case the trigonal prismatic node morphed into an octahedral node. The plausible morphing of an octahedron into a trigonal prism has already been illustrated in the case of the **soc**-MOF, where the parent **soc** net (square and octahedron) was not compatible with the trigonal prismatic node but the **soc**-derived net, **edq** net, is suitable with the trigonal prismatic SBU.¹⁷ In this case, the local geometry of the ligand is chiral like the 12-carboxylate ligand in the In-**alb**-MOF-1. The dihedral angle between the arm and the central core confers the requisite ligand geometry, compatible with the octahedrally shaped Zn(II) tetranuclear clusters present in IRMOF (isorecticular MOF) series.^{18, 29}

Fig.6 Proposed MOFs based on **alb** net and its derived net, **key** net, from the Zn(II) tetranuclear cluster and a 12-connected organic ligand. Zn, C, and O are represented by aqua, gray, and red, respectively, and H atoms and solvent molecules are omitted for clarity.

Experimental MOFs based on the shp and shp-derived nets

Encouraged by the ability of the newly designed dodecacarboxylate ligand in the In-**alb**-MOF-1 to mimic the hexagonal prism (d6R), the shp topology can be further transplanted into a copper-based MOF by the use of the copper paddlewheel [Cu₂(O₂C-) ₄] cluster³⁰ as the requisite square building unit.

As exemplified in the Fig. 7, the conformation of the linker in the Cu-**shp**-MOF-1 is comparable to the ligand conformation in the In-**alb**-MOF-1, eventually resulting in points of extension of the 12-c MBB to match the vertices of the d6R, the vertex figure of the **shp** net. The deconstruction of the ligand into one kind of 3-connected nodes and one 6-c node resulted in a structure with the novel **cez** topology: (3,4,6)-connected trinodal net with minimal transitivity [32], a new type of **shp**-derived nets.

Fig.7 Experimental MOFs based on **shp** net and its *derived* net, **cez** net, from a 4-connected Cu(II) paddlewheel cluster and a 12-connected organic ligand. Cu, C, and O are represented by green, gray, and red, respectively, and H atoms and solvent molecules are omitted for clarity.

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Proposed MOFs based on shp net and its derived nets

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Fig.8 Proposed MOFs based on **shp** net and its *derived* nets. RE, Cu, C, and O are represented by purple, green, gray, and red, respectively, and H atoms and solvent molecules are omitted for clarity. RE atoms are represented as polyhedra.

Proposed MOFs based on the **shp** and **shp-derived** nets

Following the stated rational of using minimal edge-transitive nets for the design and construction of the attained **shp**-MOFs and **alb**-MOFs, various other MOF structures based on the **shp** and **shp-derived** nets were simulated and proposed as plausible targets in MOF chemistry. Herein two illustrations regarding the **shp-derived** nets, namely **ced** net and **cee** net, were presented to support the prospective design and construction of the associated MOFs. (**Fig. 8**)

The **ced** net was derived by deconstructing the square building unit in the basic **shp** net into two symmetrical triangular building units, in combination with the d6R building unit, leading to a (3,3,12)-connected or (3,12)-connected net (two triangles are same by symmetry). In order to attain the MOF based on the **ced** net, a rectangular organic ligand containing two symmetric triangular nodes was purposely chosen to assemble with the 12-connected d6R shaped RE(III) nonanuclear cluster. The tetratopic ligand 3,3',5,5'-tetrakis(4-carboxyphenyl)-p-terphenyl (H_4TCPT) was recently reported by our group to act as a rectangular MBBs with the RE(III) cuboctahedron shaped hexanuclear clusters and Al(III) trinuclear clusters to form the **ftw**-MOF²¹ and **soc**-MOF³, respectively. It is to be noted that this linker in **ftw**-MOF and **soc**-MOF can be deconstructed into two linked triangles, resulting in the **ftw derived** net (**kle** net) and **soc derived** net (**edq** net). The proposed and the to be targeted MOF structure based on the **ced** net can be simulated, and potentially achieved, using the aforementioned ligand, embedding two symmetrical triangular nodes, in combination with RE(III) nonanuclear cluster.

On the other hand, the 12-c dodecacarboxylate ligands as the requisite hexagonal prism building unit, proposed for targeting MOFs based on **kew** net (an **alb derived** net), can be extended to simulate/target other **shp**-MOF platforms based on other *derived* nets. Reasonably, the ability of these newly simulated dodecacarboxylate ligands to mimic the d6R, by peripherally exposing the twelve carboxylates to resemble the requisite hexagonal prism building unit, with the arm perpendicular to the central benzene ring, position them as proper candidates for the prospective construction of the targeted **shp**-MOF reticulating a specific *derived* net. A copper-based MOF based on the **cee** net (an **shp derived** net) can be envisioned and potentially targeted by employing the copper paddlewheel $[Cu_2(O_2C)_4]$ cluster as the complementary square building unit in combination with the previously mentioned dodecacarboxylate ligand, as illustrated in **Fig. 8**. The

replacement of the methoxy group in the ligand of Cu-**shp**-MOF-1 (with **shp derived** net, **cez** net) by a *para*-phenylene group promotes the rigidity and the opposite steric hindrance, allowing more the peripheral arms on the linker to be perpendicular the central benzene ring. Conceivably, with a higher degree of predictability, the proposed MOF based on **cee** net can be targeted and plausibly constructed by combining the copper paddlewheel MBB and the designated d6R-like 12-c ligand.

Toolbox for MOFs with minimal edge-transitive nets based on d6R

With the aforementioned experimental and simulated MOFs based on **shp** and **alb** nets and their *derived* nets, we further proposed a toolbox for the design and construction of new MOFs based on the reticulation of minimal edge-transitive nets based on d6R building units as net-cBUs. As illustrated in **Fig. 9**, the toolbox contains two parts for both **shp** and **alb** nets, namely the plausible organic and inorganic MBBs. For example, for targeting the (4,12)-c **shp** net the material-designer can elect to choose the combination of: i) a 4-c paddlewheel cluster and a d6R shaped organic ligand, or ii) a 12-c hexagonal prismatic polynuclear metal cluster and a 4-c ligand. For the construction of MOF based on the (6,12)-c **alb** net, the material-designed can elect to combine as the net-cBUs: i) a 6-c metal cluster and a 12-c d6R organic MBB, or ii) a 6-c trigonal prismatic organic building block and a 12-c polynuclear cluster. It is to be noted that the trigonal prismatic node in the **alb** net can morph into an octahedral one. Prominently, the well-documented Zn (II) tetranuclear clusters can be potentially deployed in combination with a 12-c hexagonal prismatic linker for the prospective construction of the *derived alb*-MOF, reticulating the **key** net. It is to be noted that in the proposed 12-c polytopic linkers, the angle of the carboxylate arm can also be 90° instead of 120° as exemplified in the proposed 12-c organic ligand based on carbazole moieties (**Fig. 9**).

Toolbox for MOFs with minimal edge-transitive nets based on d6R

shp net and shp-derived nets

alb net and alb-derived nets

Fig. 9 Toolbox for the MOFs with minimal edge-transitive nets based on d6R. RE, Cu, In, Zn, C, N, and O are represented by purple, green, aqua, lime, gray, blue, and red, respectively, and H atoms and solvent molecules are omitted for clarity. RE atoms are represented as polyhedra. The newly proposed organic linkers for the shp and alb MOFs are shown in black.

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Conclusions

We reported the design and synthesis of highly-connected MOFs based on minimal edge-transitive nets, exemplified by the two binodal edge-transitive **shp** and **alb** nets and their minimal edge-transitive derived nets.

We described the procedure for obtaining derived nets from the parent highly-connected edge-transitive net (i.e. **shp** net or **alb** net) based on splitting one type of vertex into groups of linked vertices of lower coordination (e.g., one 12-c to one 6-c and one type of 3-c). The relationship of the basic net and derived net was illustrated in both simulated and experimental **shp** and **alb** MOFs in accordance with specific derived nets.

The use of minimal edge-transitive nets for the design and construction of highly coordinated MOFs has been further elaborated with the introduction of the concept of net-coded building units (**net**-cBUs), where precise embedded geometrical information codes exclusively and matchlessly a selected net. Specifically, the deliberate topological transplantation in the **alb**-MOFs illustrates the benefits of considering **net**-cBUs as a rational and feasible pathway for the design and construction of 3-periodic MOFs. Furthermore, the proposed/simulated and experimental MOF structures demonstrated the potential of deploying branched ligands as a reliable pathway for the deliberate access of the requisite and intricate highly coordinated **net**-cBUs.

Acknowledgements

Research reported in this publication was supported by King Abdullah University of Science and Technology (KAUST).

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