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

Zhijie Chen, Hao Jiang, Michael O’Keeffe and Mohamed Eddaoudi

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 diborate, 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 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.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

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

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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.\textsuperscript{19, 16, 23} Practically, we recently introduced the 12-c hexagonal prismatic (d6R) MBBs for the design and construction of MOFs based on two unique 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).\textsuperscript{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). 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 zez 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. A net augmentation 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 TBUs, leading to a related derived nets. For clarity, all topologies discussed in this contribution are represented as augmented nets.

It is to be stated that shp-a and alb-a are the only binodal edge-transitive nets embedding the hexagonal prism (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

Notably, 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. 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. 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 net
net connectivity is illustrated by \([X_m]Y[Z_n]\) 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).

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

<table>
<thead>
<tr>
<th>operation</th>
<th>symmetry</th>
<th>shp derived</th>
<th>shp CF</th>
<th>alb derived</th>
<th>alb CF</th>
</tr>
</thead>
<tbody>
<tr>
<td>X-1-3</td>
<td>(P6/m) 2</td>
<td>ced</td>
<td>(S_3[Q_3])</td>
<td>ala</td>
<td>(P_3[Q_3])</td>
</tr>
<tr>
<td>X-1-3 2c</td>
<td>(P6/m) mcm</td>
<td>cek</td>
<td>(S_3[Q_3])</td>
<td></td>
<td></td>
</tr>
<tr>
<td>X-1-3 2c</td>
<td>(P6/m) mcm</td>
<td>cee</td>
<td>(S_3[3H])</td>
<td>kew</td>
<td>(P_3[3H])</td>
</tr>
<tr>
<td>X-1-6b</td>
<td>(P622)</td>
<td>ceh</td>
<td>(T_3^* [3H])</td>
<td>key</td>
<td>(O^* [3H])</td>
</tr>
<tr>
<td>X-1-6b 2c</td>
<td>(P6/mcc)</td>
<td>cez</td>
<td>(S_3[3H])</td>
<td>kez</td>
<td>(P_3[3H])</td>
</tr>
<tr>
<td>X-1-6c 2c</td>
<td>(P6/mcc)</td>
<td>ced</td>
<td>(S_3[3O])</td>
<td></td>
<td></td>
</tr>
<tr>
<td>X-1-6c 2c</td>
<td>(P6/mcc)</td>
<td>cee</td>
<td>(S_3[3O])</td>
<td></td>
<td></td>
</tr>
<tr>
<td>X-1-6d 2c</td>
<td>(P6/mcc)</td>
<td>cet</td>
<td>(P_3[3O])</td>
<td></td>
<td></td>
</tr>
<tr>
<td>X-1-6d 2c</td>
<td>(P6/mcc)</td>
<td>cee</td>
<td>(P_3[5S])</td>
<td></td>
<td></td>
</tr>
<tr>
<td>X-3-6</td>
<td>(P6/mcc)</td>
<td>cee</td>
<td>(S_3[5S])</td>
<td>cee</td>
<td>(O^* [5S])</td>
</tr>
</tbody>
</table>

3|X-1,y,Y| represents the number of nodes in the center of this hexagonal prism and \(n\) represents the number of derived nodes between the central nodes and vertices; \[X_m]Y[Z_n]\) represents that \(Y\) is linked to \(m\) \(X\) and \(n\) \(Z\) (Fig. 2a), \([X_m]Y\) 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.

<table>
<thead>
<tr>
<th>operation</th>
<th>symmetry</th>
<th>shp derived</th>
<th>shp CF</th>
<th>alb derived</th>
<th>alb CF</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-2a</td>
<td>(P6/mmm)</td>
<td>cec</td>
<td>(3X_2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S-2b</td>
<td>(P6/mmm)</td>
<td>ced</td>
<td>(3X_2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P-2</td>
<td>(P6/mmm)</td>
<td>cen</td>
<td>(3X_2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P-3-3</td>
<td>(P6/mmm)</td>
<td>cee</td>
<td>(3X_2)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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 \(P-n_x\), \(n_x\) represents the number of nodes in the center of this trigonal prism and \(n\) represents the number of derived nodes between the central nodes and vertices. \([X_m]Y[Z_n]\) represents that \(Y\) is linked to \(m\) \(X\) and \(n\) \(Z\) (Fig. 2c), \([X_m]Y\) is derived from the parent net; \([Y]Z\) represents that \(Y\) is linked to another \(Y\) and \(Z\) (Fig. 2b and 2c), \([Y]\) is derived from the parent net; for coordination figure (CF), 3 = triangle, 5 = 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. The predesigned hexacarboxylate ligand (2,4,6-trimethyl-1,3,5-tri(3,5-di(4-carboxyphenyl-1-yl)phenyl-1-yl)-benzene (H$_6$Me-TDCPB)), provided the requisite trigonal prism and guided the occurrence of the RE hexanuclear carboxylate-based cluster \([\text{RE}_6(\mu_3\text{-OH})_8(\text{H}_2\text{O})_2(\text{O}_2\text{C}^-)_2]_{12}\) (\(\text{RE} = \text{Y}, \text{Tb}\); 2-fluorobenzoate (2-FBzoate) = C$_7$H$_4$FO$_2$) 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 \([\text{In}_3(\mu_3\text{-O})(\text{O}_2\text{C}^-)_6]_3\) 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).

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.
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 angel 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. The reported
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.
hexacarboxylate ligand 1,4-phenylenebis(tris(4-carboxyphenyl)silane) was carefully chosen from literature 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 Zn$_2$O 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 dodecarboxylate 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. 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 (isoreticular MOF) series.

Encouraged by the ability of the newly designed dodecarboxylate 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 [Cu$_2$(O$_2$C$_2$)$_4$] cluster 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, 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.
Proposed MOFs based on shp net and its derived nets

- TBU
- Square
- shp-a net (4,12)-c
- d6R
- TBU
- RE(III) nonanuclear cluster
- ced-a net (3,3,12)-c
- shp-derived net
- Network deconstruction
- cee-a net (3,4,6)-c
- shp-derived net
- Network deconstruction
- Cu(II) paddlewheel cluster

This
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′-tetakis(4-carboxyphenyl)-p-terphenyl (H4edq) 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 from 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[Cu3(O2C−)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, cee 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).
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 light and black.
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.

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Notes and references

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