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# Linker Desymmetrization: Access to a Series of Rare-Earth Tetracarboxylate Frameworks with Eight-Connected Hexanuclear Nodes

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**ABSTRACT:** The exploration of metal—organic frameworks (MOFs) through the rational design of building units with specific sizes, geometries, and symmetries is essential for enriching the structural diversity of porous solids for applications including storage, separation, and conversion. However, it is still a challenge to directly synthesize rare-earth (RE) MOFs with less connected clusters as a thermodynamically favored product. Herein, we report a systematic investigation on the influence of size, rigidity, and symmetry of linkers over the formation of RE-tetracarboxylate MOFs and uncover the critical role of linker desymmetrization in constructing RE-MOFs with eight-connected hexanuclear clusters. Our results on nine new RE-MOFs, PCN-50X (X = 1-9), indicate that utilization of trapezoidal or tetrahedral linkers provides



accesses to traditionally unattainable RE-tetracarboxylate MOFs with 8-c hexanuclear nodes, while the introduction of square or rectangular linkers during the assembly of RE-MOFs based on polynuclear clusters typically leads to the MOFs constructed from 12-c nodes with underlying **shp** topology. By rational linker design, MOFs with two unprecedented (4, 8)-c nets, **lxl** and **jun**, can also be obtained. This work highlights linker desymmetrization as a powerful strategy to enhance MOFs' structural complexity and access MOF materials with nondefault topologies that can be potentially used for separation and catalysis.

# INTRODUCTION

Ligand design plays an essential role in the prediction and construction of metal-organic frameworks (MOFs) with ideal pore environments for applications including separation, storage, and conversion.<sup>1–6</sup> Through rational design of building blocks with specific sizes, geometries, and symmetries, framework materials with predetermined topologies and optimized pore spaces can be accessed.<sup>7,8</sup> For instance, Yaghi and coworkers adjusted symmetry of a ditopic linker, 4,4'-biphenyldicarboxylate (bpdc), by altering the locations of linker substituents to control the formation of a two-dimensional MOF-118 and a three-dimensional MOF-601.<sup>9</sup> In MOF-118, the two carboxylate-group planes are close to coplanar, while they are perpendicular to each other in MOF-601 due to the bulk of the linker substitutes. A similar concept has also been introduced into Zr-MOFs later, for example, the formation of UiO-67 with coordinatively saturated clusters and PCN-700 with open pockets that allow for the installation of linkers with varying lengths and combinations.<sup>10</sup> Recently, Guillerm, Maspoch, and co-workers provided a summary on this topic, where they described a "geometry mismatch" concept to assemble MOFs with nondefault topologies.<sup>11</sup> These progresses provide fresh insights into the design of complex MOFs with

unusual topologies and properties for applications in sensing, catalysis, and separation.  $^{12-14}\,$ 

Among metals utilized for MOF construction, rare-earth (RE) elements have recently attracted increasing attention because they can form more adaptable RE polynuclear clusters including RE<sub>6</sub>, RE<sub>4</sub>, RE<sub>9</sub>, and RE<sub>18</sub> clusters that can function as building blocks for the assembly of diverse topologies with high connectivity.<sup>15</sup> Notably, there are some similarities between Zr-MOFs and RE-MOFs; for example, **fcu** topology can be found in both Zr-MOFs and RE-MOFs when linking  $[Zr_6(\mu_3 - O)_4(\mu_3 - OH)_4]$  or  $[RE_6(\mu_3 - OH)_8]$  clusters with ditopic linkers, respectively.<sup>16–19</sup> Yet, one major difference between Zr-MOFs and RE-MOFs is that less connected clusters are rarely observed in RE-MOFs but are common in Zr-MOFs. For example, when the tritopic linker BTB<sup>3–</sup> is involved, Zr-BTB interpenetrated

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networks or nanosheets with 6-c  $\operatorname{Zr}_6$  cluster are obtained<sup>20,21</sup> while gea-MOF-1(RE) crystals with fully coordinated 18-c RE<sub>9</sub> clusters are assembled, without the observation of less connected RE clusters.<sup>22</sup> When the tritopic linker TATB<sup>3-</sup> is involved, PCN-777 crystals with 6-c Zr<sub>6</sub> cluster are obtained,<sup>23</sup> while sph-MOF-4(RE) crystals can only form with the assistance of a secondary tritopic linker, which ensures the formation of fully coordinated 12-c RE<sub>6</sub> clusters.<sup>24</sup> The reason behind this phenomenon is because the RE cation allows for multiple directionality of coordinated ligands, and each cation can coordinate with 6-12 terminal ligands, while the coordinate number of Zr cation is eight.  $^{25-27}$  Therefore, the less connected RE clusters will inevitably destabilize the framework and usually lead to the formation of other thermodynamically favored products. A typical example is PCN-900(RE) constructed from TCPP<sup>4-</sup> linkers.<sup>28</sup> In Zr-MOFs, there are multiple phases including PCN-222 with 8-c  $Zr_6$  clusters and PCN-224 with 6-c Zr<sub>6</sub> clusters formed during the assembly of Zr clusters and TCPP linkers. However, these structures are inaccessible in RE-MOFs without the addition of an auxiliary linker to fulfill the fully connected RE clusters.

Most reported RE-MOFs constructed from tetratopic linkers contain fully connected RE clusters. Eddaoudi and co-workers employed a series of square and rectangular linkers during the synthesis of RE-MOFs and obtained MOFs with 4,12-c ftw and 4,12-c shp topologies.<sup>29-31</sup> Li and co-workers further introduced two rectangular linkers to assemble RE-MOFs for separation.<sup>32,33</sup> MOFs with ftw topology were harvested; however, the MOF with predicted 4,8-c scu topology was failed to fabricate, showing the challenges lying in the direct synthesis of RE-MOFs with less connected RE clusters. Very recently, Trikalitis and co-workers reported two RE-MOFs based on tetrahedral linkers: 4,12-c RE-hpt-MOF-1 and 4,8-c RE-ken-MOF-1.34 Further development of RE-MOFs with less connected RE clusters requires enhanced understanding on the influence of linker symmetry over the formation of frameworks.<sup>35</sup> Herein, we uncover the importance of linker desymmetrization in accessing RE-tetracarboxylate MOFs with 8-connected RE<sub>6</sub> clusters. Structural studies of nine new MOFs, PCN-50X (X = 1-9), constructed from tetracarboxylate linkers with varying sizes, rigidities, and symmetries reveal that utilization of trapezoidal or tetrahedral linkers provides accesses to traditionally unattainable RE-tetracarboxylate MOFs with 8-c hexanuclear nodes. The introduction of square or rectangular linkers during the assembly of RE-MOFs based on polynuclear clusters typically leads to the MOFs constructed from 12-c nodes with underlying shp topology. By rational linker design, MOFs with unprecedented (4, 8)-c nets including lxl and jun can also be obtained (Figure 1). This work highlights the role of linker desymmetrization in accessing MOF materials with nondefault topologies, which can function as a powerful strategy to enhance structural complexity of MOFs. The potentially unsaturated metal sites within these 8-connected hexanuclear nodes can be used for guest binding during separation and catalysis processes.

# RESULTS AND DISCUSSION

**RE-Tetracarboxylate MOFs Based on Rectangular Linkers.** Herein we selected nine tetratopic linkers with various sizes, rigidities, and symmetries to explore the structures and topologies of RE-MOFs (Figure 2). With the modulation of 2fluorobenzoic acid (2-FBA), solvothermal reactions between rectangular H<sub>4</sub>L1 and Eu(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O for 48 h yielded large



**Figure 1.** Reported topologies (**ftw**, **shp**, **flu**, and **hjz**) and newly discovered topologies (**scu**, **kl**, and **jun**) in RE-tetracarboxylate MOFs built on  $RE_6$  or  $RE_9$  clusters.



**Figure 2.** Tetracarboxylate linkers (L1–L9) with different sizes, rigidities, and symmetries used in this work.

PCN-501 crystals with a shp topology. It contains a 12connected  $[RE_9(\mu_3-OH)_{12}(\mu_3-O)_2(O_2C-)_{12}]$  cluster as a hexagonal prism node and a tetratopic linker as a joint rectangular node. Additionally, under the same condition, the reaction between Eu(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and H<sub>4</sub>L2 also yields PCN-502 crystals with the same topology because of the same conformations and geometries of  $L1^{4-}$  and  $L2^{4-}$ . It should be noticed that the Tb and Y-based MOFs with shp topology, named CU-10, have been recently reported by Howarth and coworkers.<sup>37</sup> This observation is consistent with previous reports that the introduction of a rectangular linker into 2-FBA modulated RE-MOFs will generate a shp topology (Figure 3). Saturated N<sub>2</sub> uptakes of 652 and 517 cm<sup>3</sup> g<sup>-1</sup> (STP) are achieved, and the BET surface areas of PCN-501 and -502 are estimated to be 2277 and 1978  $m^2\,g^{-1}$  , respectively (Figures S32 and S33). The pore volumes are calculated to be 1.01 and 0.80  $cm^3 g^{-1}$ , respectively.

**RE-Tetracarboxylate MOFs Based on Tetrahedral Linkers.** To study the effects of linker geometry over structural formation, methyl groups are added onto the two central phenyl rings in the examples of  $H_4L3$  and  $H_4L4$ . This modification

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**Figure 3.** Structures and topologies of PCN-50X (X = 1-4). (a) Linking of 4-c rectangular linkers (L1 and L2) with 12-connected RE<sub>9</sub> clusters leads to the formation of PCN-501 and PCN-502 (**shp** topology). (b) Employment of 4-c tetrahedral linkers (L3 and L4) prompts the formation of PCN-503 and PCN-504 (**flu** topology) constructed from 8-connected RE<sub>6</sub> clusters. RE, C, O, and N atoms are represented by turquoise, gray, red, and blue, respectively, and H atoms are omitted for clarity.



**Figure 4.** Structures and topologies of PCN-50X (X = 5, 6). (a) Organic linkers rectangular L5 and trapezoidal L6 display different geometries in extended frameworks. (b) Structural illustration of PCN-505 and PCN-506. (c) Underlying **scu** and **shp** topologies of PCN-505 and PCN-506, respectively. RE, C, O, and N atoms are represented by turquoise, gray, red, and blue, respectively, and H atoms are omitted for clarity.

alters the original rectangular geometry into a tetrahedral shape. The assembly of tetrahedral  $H_4L3/H_4L4$  and hexanuclear RE clusters prompts the formation of PCN-503/504 with a (4,8)-c **flu** topology (Figure 3). In these two cases, the linker  $L3^{4-}/L4^{4-}$ 



**Figure 5.** Proposed formation mechanism of different topologies using L5 and L6. (a) Installation of rectangular linkers into frameworks based on **scu** net leads to the formation of PCN-505 with a **shp** net. (b) A **scu** net can also form by using a trapezoidal building unit; however, it does not allow for the installation of trapezoidal building blocks into the open pockets due to size mismatch.

were considered to be very rigid linkers due to the presence of the 2,2',6,6'-tetramethylbiphenyl core. Because of the steric hindrances of neighboring methyl groups, the orientation of the two central phenyl rings is strongly constrained. The clusters were found to be 8-connected RE<sub>6</sub> clusters, similar to 8-c Zr<sub>6</sub> clusters in widely studied Zr-MOFs. Saturated N<sub>2</sub> uptakes of 632 and 485 cm<sup>3</sup> g<sup>-1</sup> (STP) are achieved, and the BET surface areas of PCN-503 and -504 are estimated to be 2715 and 1616 m<sup>2</sup> g<sup>-1</sup>, respectively (Figures S34 and S35). The pore volumes are calculated to be 0.98 and 0.76 cm<sup>3</sup> g<sup>-1</sup>, respectively.

RE-Tetracarboxylate MOFs Based on Trapezoidal Linkers. RE-MOFs based on linkers with a reduced symmetry, such as a trapezoidal shape, have not been fully investigated yet. When replacing the pyrene core with a carbazole core in the tetracarboxylates, the linker symmetry can be decreased to  $C_s$ accordingly. Solvothermal reactions between  $Eu(NO_3)_3 \cdot 6H_2O$ and trapezoidal linker H<sub>4</sub>L5 in the presence of 2-FBA for 48 h yielded large colorless crystals, PCN-505 with a (4, 12)-c shp topology (Figure 4c). It is traditionally observed that the selection of contracted or expanded linkers will not alter the underlying topology of a MOF structure under the same reaction conditions.<sup>36</sup> However, in this case, the employment of its contracted version L6<sup>4-</sup> prompts the formation of PCN-506 with a different (4, 8)-c scu topology in RE-MOFs. To the best of our knowledge, this topology has not been discovered in RE-MOFs, although it is common in Zr-MOFs. Single-crystal X-ray diffraction (SCXRD) provides direct information about the geometry of  $L5^{4-}/L6^{4-}$  in the MOF structures, which allows for the investigation of formation mechanism of different top-

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**Figure 6.** Topological comparison between (6, 12)-c **alb** net and (4, 8)-c **lxl** net. (a) Use of a 6-c triangular prism linker (disordered L7) resulted in the formation of disordered PCN-507 with underlying **alb** topology. (b) Utilization of a 4-c tetrahedral linker (L7) resulted in the discovery of PCN-507 with a new **lxl** topology. RE, C, O, and N atoms are represented by turquoise, gray, red, and blue, respectively, and H atoms are omitted for clarity.



**Figure 7.** Schemes showing structures and topologies of PCN-507 with and without disorder. (a) Insertion of 6-c triangular prism linkers between hxl RE<sub>6</sub> layers results in the assembly of disordered PCN-507 with **alb** topology. (b) Introduction of 4-c tetrahedral linkers between hxl RE<sub>6</sub> layers can induce the formation of PCN-507 with lxl topology. RE, C, O, and N atoms are represented by turquoise, gray, red, and blue, respectively, and H atoms are omitted for clarity.

ologies. It was found that the rigid  $L6^{4-}$  linker with shorter benzoate arms displays a trapezoidal geometry while the flexible  $L5^{4-}$  linker with longer naphthoate arms displays a rectangular geometry in the constrained framework. From a topological perspective, the formation of a **shp** net can be viewed as a result of installation of rectangular building blocks into the open pockets in a **scu** net (Figure 5a). Because of the preference for RE clusters to be fully coordinated, structures with **shp** topology formed eventually as a thermodynamic favorable product. However, trapezoidal building blocks cannot be solely used for the construction of a **shp** net because the installation of trapezoidal building blocks into the open pockets of a **scu** net is prohibited due to size mismatch. This explains the importance of linker desymmetrization in accessing RE-MOFs with relatively low connectivity. Saturated N<sub>2</sub> uptakes of 612 and 446 cm<sup>3</sup> g<sup>-1</sup> (STP) are achieved, and the BET surface areas of PCN-505 and -506 are estimated to be 2401 and 1766 m<sup>2</sup> g<sup>-1</sup>, respectively (Figures S36 and S37). The pore volumes are calculated to be 0.96 and 0.69 cm<sup>3</sup> g<sup>-1</sup>, respectively.

**RE-Tetracarboxylate MOFs Based on Distorted Tetrahedral Linkers.** Further reduction of linker symmetry by removing naphthoate units in two side arms was conducted in linker  $L7^{4-}$ . The free rotation of two other side arms endows the linker with a distorted tetrahedral shape. Use of the tetrahedral



**Figure 8.** Structural and topological analysis of PCN-50X (X = 8, 9). (a) Use of a 4-c distorted tetrahedral linker (L8 and L9) resulted in the formation of PCN-508 and PCN-509 with underlying **jun** topology. (b) Structural illustration of PCN-508 and PCN-509. (c) RE<sub>6</sub> **hxl** layers A and B, perpendicular to each other, allow for the installation of L8 or L9 to form a 3D pillar-layered structure. (d) Structural comparison between PCN-507 and PCN-508: a pair of  $L7^{4-}(\alpha \text{ and } \beta)$  linkers are linked to seven RE<sub>6</sub> clusters in PCN-507 while a pair of  $L8^{4-}(\alpha \text{ and } \beta)$  linkers are only connected to six RE<sub>6</sub> clusters in PCN-508. RE, C, O, and N atoms are represented by turquoise, gray, red, and blue, respectively, and H atoms are omitted for clarity.

 $L7^{4-}$  linker resulted in the discovery of PCN-507 with a new (4, 8)-c lxl topology derived from (6, 12)-c alb topology. Reactions between  $Eu(NO_3)_3$ ·6H<sub>2</sub>O and H<sub>4</sub>L7 in the presence of 2-FBA yielded colorless PCN-507 crystals. The SCXRD structure indicated that PCN-507 crystallizes in the Cmcm space group. It should be noted that a 6-connected linker (disordered L7) was observed as a result of crystallographic disorder, which has also been observed previously.<sup>38,39</sup> Topological analysis of the resulting crystal structure reveals that it reticulates the (6.12)c alb net, containing a 12-c Eu<sub>6</sub> cluster as a hexagonal prism node and a 6-c disordered linker as a triangular prism node. Alternatively, PCN-507 structure can be viewed as a pillarlayered structure. The hexanuclear RE clusters are placed into hxl layers while disordered L7 linkers as pillars are inserted between layers to form a 3-periodic MOF (Figure 7a). To unveil more structural information, the crystallographic disorder of the  $L7^4$  linker was removed by only selecting four intrinsic carboxylates on each L7<sup>4-</sup> linker. As shown in Figure 6b, PCN-507 without disorder contains an 8-connected Eu<sub>6</sub> cluster and a 4-connected distorted tetrahedral linker. The overall structure was found to be a new 4,8-connected lxl net with a point symbol of  $\{4^{12}.6^8.8^8\}\{4^4.6^2\}^4\{4^6.6^{18}.8^4\}$  as determined by TOPOS 4.0 (Figure 7b).<sup>40</sup> In this case, the structure can be viewed as a result of the installation of tetrahedral L7 pillars between hxl layers consisting of RE<sub>6</sub> clusters. The largest diamondoid channels in PCN-507 are along the crystallographic b direction and relatively small ones in the c directions; the lengths are estimated to be ca. 8 and 12 Å, respectively. Saturated  $N_2$  uptakes of 378  $\mbox{cm}^3\mbox{ g}^{-1}$  (STP) are achieved, and the BET

surface area of PCN-507 is estimated to be 1408 m<sup>2</sup> g<sup>-1</sup> (Figure S38). The pore volumes are calculated to be 0.57 cm<sup>3</sup> g<sup>-1</sup>.

Replacement of the central phenyl core in H<sub>4</sub>L7 with a carbazole core leads to the generation of H<sub>4</sub>L8, altering the angle between naphthoate groups on the core from  $120^{\circ}$  to  $90^{\circ}$ . Solvothermal reactions between  $H_4L8$  and  $Eu(NO_3)_3 \cdot 6H_2O$  in the presence of 2-FBA for 48 h yielded crystals of PCN-508 (Figure 8a,b). PCN-508 crystallized in the C2/c space group (Table S6). Crystallographically, it contains a 8-connected  $RE_6$ cluster and a distorted tetrahedral linker (Figure 2c,d). The overall structure was analyzed to be a new 4,8-connected jun net with a point symbol of  $\{4^4.6^2\}^2\{4^8.6^{17}.8^3\}$  as determined by TOPOS 4.0. Because of the changes on the linker conformation, the connectivity mode in PCN-507 and PCN-508 varies. As shown in Figure 8d, a pair of  $L7^{4-}(\alpha \text{ and } \beta)$  linkers are linked to seven RE<sub>6</sub> clusters in PCN-507 while a pair of L8<sup>4–</sup>( $\alpha$  and  $\beta$ ) linkers are only connected to six RE<sub>6</sub> clusters in PCN-508. Moreover, four clusters linked by one linker are parallel to each other in PCN-507. Yet, in PCN-508, the orientation of four clusters linked by one linker is different: two of them are perpendicular to the other two. As a result, there are two types of  $RE_6$  hxl layers (A and B, Figure 8c) existing in the pillar-layered structure. Utilization of  $L9^{4-}$  linker with shorter benzoate arms generates isoretcular PCN-509 with jun topology due to the similarity of geometry and rigidity between L8<sup>4-</sup> and L9<sup>4-</sup>. The shape of the channels observed in PCN-508 and -509 is diamondoid; the lengths are estimated to be ca. 12 and 7 Å, respectively, which match well with the actual size observed in the pore size distribution (Figures S39 and S40) Saturated N<sub>2</sub> uptakes of 412 and 316  $\text{cm}^3 \text{g}^{-1}$  (STP) are achieved, and the

BET surface areas of PCN-508 and -509 are estimated to be 1549 and 1170 m<sup>2</sup> g<sup>-1</sup>, respectively. The pore volumes are calculated to be 0.65 and 0.49 cm<sup>3</sup> g<sup>-1</sup>, respectively.

Stability and Porosity. The permanent porosity of the PCN-50X(Eu) series was revealed by N<sub>2</sub> sorption isotherms measured at 77 K, indicating their microporous features (section 5 in the Supporting Information). The chemical stability of the PCN-50X series was further assessed by immersing them into varying solvents for 24 h. As indicated by the corresponding PXRD patterns, the PCN-50X(Eu) series was stable in water and most organic solvents including acetone, dichloromethane, acetonitrile, and methanol (Figures \$14-\$31). The preparation of PCN-50X series based on other RE metals such as Y and Yb was also conducted under similar solvothermal reaction conditions, with PXRD patterns showing their phase purities (Figures S14–S31). Overall, our systematic research on the REtetracarboxylate frameworks sheds light on the precise design and synthesis of organic ligands for the assembly of porous MOF structures and shall accelerate the discovery of highly connected networks with unprecedented topologies. Further studies of these potentially unsaturated RE metal sites within the hexanuclear nodes in separation and catalysis are currently ongoing.

## CONCLUSIONS

In conclusion, we report a design strategy, linker desymmetrization, and its utilization in preparing a series of REtetracarboxylate MOFs with 8-connected hexanuclear nodes. Depending on the size, rigidity, and symmetry of linkers, various topologies can be targeted with diverse connectivity modes. The general conclusion we reach is that utilization of square or rectangular linkers typically provides accesses to RE-MOFs based on 12-c polynuclear clusters with underlying ftw or shp topology, while the introduction of trapezoidal or tetrahedral linkers during the assembly of RE-MOFs typically leads to the MOFs constructed from 8-c hexanuclear clusters with underlying scu, flu, lxl, or jun topology. This work provides efficient design strategies for the construction of unprecedented topologies through linker desymmetrization, which shall further guide the discovery of MOF materials with nondefault topologies and unusual structural complexity. The potentially unsaturated RE sites in aforementioned MOFs are expected to allow for the installation of a secondary linker and show enhanced interaction with guest molecules, providing access to highly efficient storage, separation, sensing, and catalysis.

# ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.0c11546.

Text, tables, and figures giving experimental procedures for the syntheses of the ligands, PXRD, gas sorption isotherms, <sup>1</sup>H NMR spectra, and other additional information (PDF)

X-ray crystallographic details of PCN-50X (X = 2-9) (CIF)

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# Notes

The authors declare no competing financial interest.

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