

Sequential Linker Installation: Precise Placement of Functional Groups in Multivariate Metal–Organic Frameworks

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S Supporting Information

ABSTRACT: A unique strategy, sequential linker installation (SLI), has been developed to construct multivariate MOFs with functional groups precisely positioned. PCN-700, a Zr-MOF with eight-connected $Zr_6O_4(OH)_8(H_2O)_4$ clusters, has been judiciously designed; the Zr_6 clusters in this MOF are arranged in such a fashion that, by replacement of terminal OH^-/H_2O ligands, subsequent insertion of linear dicarboxylate linkers is achieved. We demonstrate that linkers with distinct lengths and functionalities can be sequentially installed into PCN-700. Single-crystal to single-crystal transformation is realized so that the positions of the subsequently installed linkers are pinpointed via single-crystal X-ray diffraction analyses. This methodology provides a powerful tool to construct multivariate MOFs with precisely positioned functionalities in the desired proximity, which would otherwise be difficult to achieve.

As an inorganic and organic hybrid material, metal–organic framework (MOF) epitomizes an ideal tunable structure through judicious selection of metal nodes, organic linkers, as well as the combination and modification thereof.¹ Placing two or more functionalities having synergistic effects of various kinds within one framework is particularly interesting for its many potential applications.² A ubiquitous approach to introduce multiple functionalities into MOFs is the one-pot synthesis with mixed linkers.³ One of the representative examples of this is the synthesis of MTV-MOFs (multivariate MOFs), conducted by Yaghi and co-workers, in which up to eight linear linkers having the same length but distinct functionalities were introduced into one framework.⁴ Evidence was presented that linkers of similar length and connectivity tend to be incorporated into one mixed-linker framework, rather than a mechanical mixture of single-linker MOFs. Controlled placement of functional groups is crucial for expanding the functions of MTV-MOFs. For example, these properly juxtaposed functional groups can potentially mimic delicate enzymatic systems.⁵ Further efforts were made to elucidate the spatial apportionments of functional groups by solid-state NMR and molecular simulation. However, it is still a challenge to locate the exact position of each component due to the disordered distribution of functional groups.⁶

One way to control the arrangement of functionalities is to use linkers with different symmetry and/or connectivity.⁷ If topology compatibility is satisfied, an ordered arrangement of

different linkers becomes feasible. In this case, functional groups can be found by single-crystal X-ray crystallography. Recently, this has been demonstrated by copolymerizing multiple topologically distinct linkers to produce isorecticular sets of MOFs with systematically modulated pore architectures.⁸ However, some potential limitations remain with this strategy. First, it is extremely difficult to introduce more than two linkers simultaneously into one framework, as linkers of distinct size and connectivity tend to form different domains instead of one uniform phase.⁹ In addition, it requires extra effort to maintain the integrity of certain sensitive functional groups under the harsh solvothermal conditions (i.e., functional group protection and deprotection).¹⁰ Moreover, this approach so far has only been reported as successful for soft Lewis acidic metal species (M^{2+}).^{7,11} The resulting structures usually exhibit limited chemical stability, which restricts their applications.

In this sense, the Zr_6 cluster is an excellent building unit for MTV-MOFs because of its exceptional stability and tunable connectivity.¹² Nevertheless, Zr-MOFs based on multiple linkers with different lengths, to the best of our knowledge, have never been reported. We attempted to synthesize mixed-linker Zr-MOFs starting from any combinations of BDC, BPDC, and TPDC (BDC = 1,4-benzenedicarboxylate, BPDC = 4,4'-biphenyldicarboxylate, TPDC = *p*-terphenyl-4,4''-dicarboxylate) through a one-pot synthetic approach; however, a mixture of known phases (i.e., UiO-66, UiO-67, and UiO-68) was always obtained.¹³ In one-pot synthesis, the competition between kinetically favored and thermodynamically favored products makes it exceedingly challenging to achieve mixed-linker MOF products. In order to synthesize mixed-linker Zr-MOFs, we propose a kinetically controlled synthetic strategy: namely, sequential linker installation (SLI). In this strategy, a prototype MOF (PCN-700, PCN = porous coordination network) with eight-connected $Zr_6O_4(OH)_8(H_2O)_4$ clusters is designed. Zr_6 clusters in this MOF are lined up such that the terminal OH^-/H_2O ligands on each Zr_6 cluster pairs can be removed¹⁴ to create natural “pockets” for the accommodation of linear dicarboxylate linkers with suitable lengths. There are two types of “pockets” in PCN-700, each fitting a linker with a different length. Satisfying the necessary requirements of adequate flexibility and stability, the SLI strategy has been successfully executed on PCN-700, creating a mixed-linker Zr-MOF with three linkers of different lengths. In contrast to the one-pot approach, SLI is a kinetically controlled process; the

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terminal $\text{OH}^-/\text{H}_2\text{O}$ coordinated Zr sites in the prototype MOF are more susceptible to replacement by subsequently added linkers because the activation energy is lower than that of forming a new phase.^{14b} As a result, a kinetically favored product is generated, which would otherwise be difficult to obtain by the traditional one-pot reactions. SLI is a prospective strategy to synthesize MTV-MOFs with functional groups precisely located in the framework. The resulting Zr-MOFs would be of great significance in terms of practicality because of their stability; furthermore, SLI is performed under mild conditions postsynthetically, which provides a potential venue to introduce sensitive functional groups into robust MOF frameworks.¹⁵

In order to obtain the prototype MOF, a topology-guided linker design strategy is adopted.¹⁶ The combination of a Zr_6 cluster and a linear linker usually gives rise to an **fcu** net in which the Zr_6 cluster is fully connected by linkers, leaving no room for further linker installation.¹⁷ To address this, a **bcu** net is selected as the target topology for the prototype MOF.¹⁸ A **bcu** net is composed of 8-connected cubic nodes which can be viewed as a deduction from an **fcu** net by deleting four linkers in the equatorial plane of the octahedral Zr_6 cluster (Figure 1).

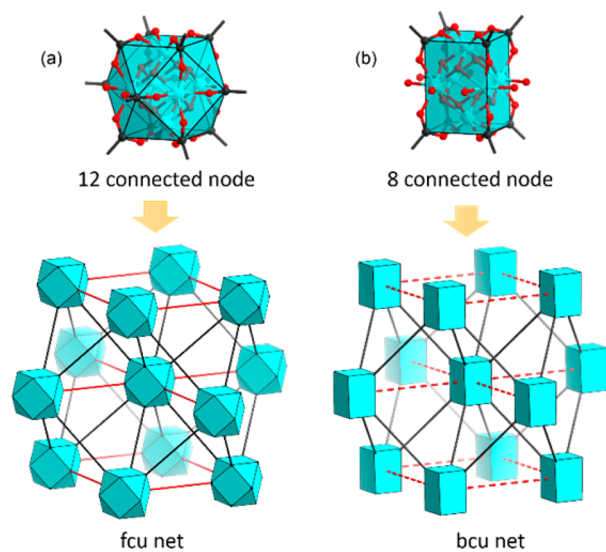


Figure 1. (a) **fcu** net formed by 12-connected nodes. (b) **bcu** net formed by 8-connected nodes.

These uncoordinated sites in a **bcu** net are well poised for subsequent linker installation. However, the reactions between Zr^{4+} ions and linear linkers such as BDC, BPDC, and TPDC always yield a 12-connected **fcu** net (UiO-66, UiO-67, and UiO-68, respectively) under solvothermal conditions, probably because a high-connectivity network is thermodynamically favored in comparison to the low-connectivity networks. It has been well demonstrated that MOF topology can be tuned by the linker configuration; therefore, we expect that a **bcu** structure could be obtained through judicious linker design.¹⁹ We reasoned that the **bcu** net could be realized if the two carboxylate groups of the linear linker were twisted off the coplanar position (Figure 2b). As shown in Figure 2c, the two carboxylate groups of the linker are required to be in the same plane in order to form a 12-connected **fcu** structure. With the twisted linker, a **bcu** net (Figure 2f) should be expected as opposed to an **fcu** net (Figure 2e). To verify our hypothesis, two methyl groups were introduced at the 2- and 2'-positions

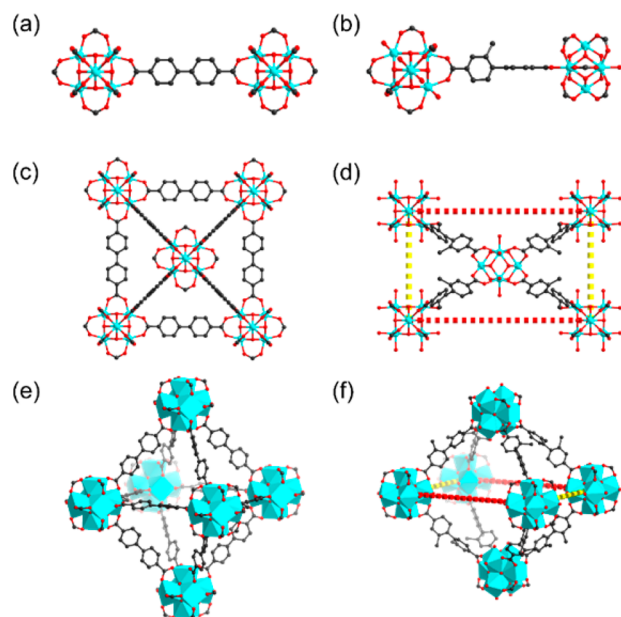


Figure 2. (a) Conformation of BPDC in the **fcu** structure. (b) Conformation of $\text{Me}_2\text{-BPDC}$ in the **bcu** structure. (c, e) **fcu** structure formed with BPDC. (d, f) **bcu** structure formed with $\text{Me}_2\text{-BPDC}$.

of the BPDC linker. Since the dihedral angle of biphenyl rings in BPDC is known to be directly related to the size and nature of substituents on the 2- and 2'-positions, the $\text{Me}_2\text{-BPDC}$ (2,2'-dimethylbiphenyl-4,4'-dicarboxylate) is expected to provide two off-plane carboxylate groups.^{19b} As expected, the reaction of $\text{H}_2\text{Me}_2\text{-BPDC}$ and ZrCl_4 in *N,N*-dimethylformamide (DMF) at 120 °C yielded crystals of the desired MOF with 8-connected topology, designated as PCN-700.

A single-crystal X-ray diffraction study reveals that PCN-700 crystallizes in the tetragonal crystal system with a $P4_2/mmc$ space group. Each Zr_6 cluster is connected to eight $\text{Me}_2\text{-BPDC}$ linkers above and below the equatorial plane and eight terminal $\text{OH}^-/\text{H}_2\text{O}$ groups in the equatorial plane (Figure 1b). The space between two adjacent Zr_6 clusters in the equatorial plane is a natural “pocket” for the accommodation of one linear dicarboxylate linker by replacing the terminal $\text{OH}^-/\text{H}_2\text{O}$ via an acid–base reaction. There are two pockets of different sizes in PCN-700 (Figure 3, pocket A and pocket B), which make it possible to sequentially install two linkers of different lengths. BDC and $\text{Me}_2\text{-TPDC}$ ($\text{Me}_2\text{-TPDC}$ = 2',5'-dimethylterphenyl-4,4''-dicarboxylate) were selected on the basis of our observation that the lengths of linkers (6.9 and 15.2 Å for BDC and $\text{Me}_2\text{-TPDC}$, respectively) match the distances between the nearest oxygens of adjacent Zr_6 clusters well (16.4 Å for pocket A and 7.0 Å for pocket B, respectively). Meanwhile, the dihedral angle of biphenyl rings is flexible (from 78.1 to 89.5°), which endows the framework with certain flexibility and allows the structure to self-adjust according to the linkers.²⁰ In addition, PCN-700 is highly stable; it retains single crystallinity during the subsequent linker installation, which enables us to employ single-crystal X-ray crystallography to pinpoint these installed functional groups. The excellent stability also ensures that the obtained MTV-MOFs will be stable and usable under relatively harsh conditions. Overall, the inherent “pockets”, flexibility, and high stability make PCN-700 an optimal platform for implementing the SLI strategy.

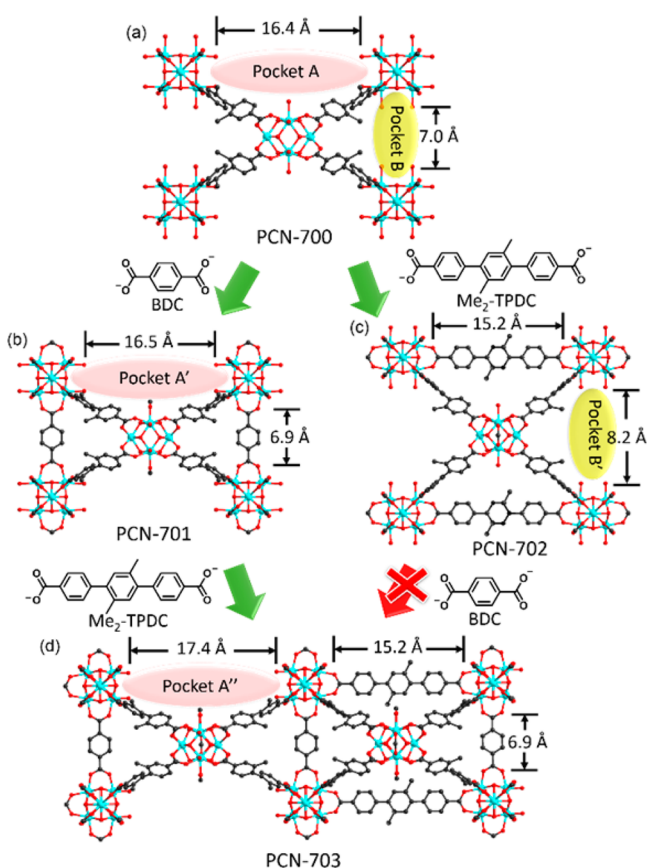


Figure 3. Structures of (a) PCN-700, (b) PCN-701, (c) PCN-702, and (d) PCN-703.

To carry out SLI, PCN-700 crystals were sequentially exposed to solutions of H_2BDC and $\text{H}_2\text{Me}_2\text{-TPDC}$ in DMF at 75 °C for 24 h. The crystals afforded were washed with fresh DMF before X-ray single-crystal diffraction data collection. The existence and position of BDC and $\text{Me}_2\text{-TPDC}$ are unambiguously observed in the crystallographically resolved structure. The resultant structure, designated as PCN-703 (Figure 3d), crystallizes in the $P4_2/mnm$ space group. Interestingly, the unit cell of PCN-703 is doubled in size compared to the prototype MOF (PCN-700) due to the asymmetric distribution of $\text{Me}_2\text{-TPDC}$ linker. In PCN-703, each Zr_6 cluster is 11-connected to eight $\text{Me}_2\text{-BPDC}$, two BDC, and one $\text{Me}_2\text{-TPDC}$ linkers. The overall composition can be formulated as $\text{Zr}_6\text{O}_4(\text{OH})_5(\text{H}_2\text{O})(\text{Me}_2\text{-BPDC})_8\text{BDC}_2(\text{Me}_2\text{-TPDC})$, which has been further confirmed by ^1H NMR. The bulk material maintains its crystallinity and porosity after SLI, which is supported by well-retained powder X-ray diffraction patterns (Figure S6 in the Supporting Information) and N_2 gas adsorption–desorption isotherms (Figure S13 in the Supporting Information).

It should be noted that the sequence of the installation is crucial for the success of SLI. As shown in Figure 3, starting with a short linker, the BDC will occupy all the small pockets (pocket B) with an O...O distance of 7.0 Å, leaving the large pockets (pocket A') unoccupied. Pocket A' has an O...O distance of 16.5 Å, which is slightly longer than the size of $\text{Me}_2\text{-TPDC}$ (15.2 Å). Further incorporated $\text{Me}_2\text{-TPDC}$ will only occupy every other pocket A' and stretch the other pocket A' to 17.4 Å (pocket A''). As a result, a MOF with three linkers of different lengths is obtained. However, if the $\text{Me}_2\text{-TPDC}$

linkers are installed first, they will occupy all the pockets A and meanwhile stretch the pocket B to 8.2 Å (pocket B'). Therefore, it is impossible to install BDC into these elongated pockets (pocket B') because the length of BDC is only 7.0 Å.

With the successful stepwise synthesis of PCN-703, we believe functionalized linkers should also be usable for this strategy and the resulting MTV-MOFs should possess the same topology as long as the lengths of linkers are not altered. As a proof of concept, two functionalized linkers, $\text{NH}_2\text{-BDC}$ (2-amino-1,4-benzenedicarboxylate) and $(\text{CH}_3\text{O})_2\text{-TPDC}$ (2',5'-dimethoxyterphenyl-4,4''-dicarboxylate), were installed using the SLI strategy, which gave rise to a new MTV-MOF, namely PCN-704. It exhibits topology identical with that of PCN-703. Single-crystal X-ray crystallography and ^1H NMR clearly indicate the existence and proper ratio of $\text{NH}_2\text{-BDC}$ and $(\text{CH}_3\text{O})_2\text{-TPDC}$. By using the SLI strategy, we successfully demonstrated an ordered MTV-MOF fabrication with amino groups, methoxyl groups, and methyl groups precisely arranged.

In summary, we have developed a unique strategy, sequential linker installation (SLI), to construct multivariate MOFs with functional groups precisely located. Single-crystal to single-crystal transformation has been realized, and the positions of the subsequently installed linkers have been pinpointed. SLI is a powerful methodology to introduce multiple functional groups into MOFs in a controlled and crystallographically ordered manner, particularly for those based on hard Lewis acidic metal species. In light of their structural adaptability and high chemical stability, we anticipate SLI will have a variety of applications, especially when specific functional groups in the proper proximity are desired.

■ ASSOCIATED CONTENT

📄 Supporting Information

Text, tables, and figures giving experimental procedures for the syntheses of the ligand, PXRD, N_2 adsorption isotherms, ^1H NMR spectra, and crystallographic data of the structure. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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