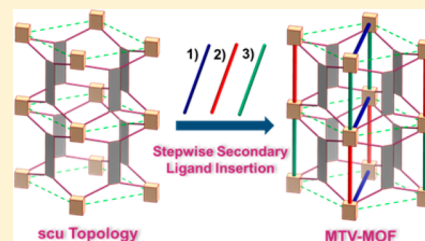


## Topology-Guided Stepwise Insertion of Three Secondary Linkers in Zirconium Metal–Organic Frameworks

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## Supporting Information

**ABSTRACT:** We report a topology-guided, precise insertion of three distinct secondary linkers into a zirconium-based metal–organic framework, NPF-300. Constructed from a tetratopic linker **L** and  $\text{Zr}_6$  cluster, NPF-300 exhibits a unique *scu* topology and certain flexibility along the crystallographic *a* axis, and in conjunction with the conformation change of the primary ligand, is able to accommodate the stepwise insertion of three different secondary linkers along the *a* and *c* axes. Size-matching and mechanic strain of the resulting framework are two important factors that determine the chemical stability of the inserted linkers. Secondary linker insertion in NPF-300 significantly enables not only its porosity but also potentials to install up to three different functional groups for the construction of multivariate MOFs with homogeneity.



## INTRODUCTION

Metal–organic frameworks (MOFs) are inorganic–organic hybrid materials constructed via the self-assembly of judiciously selected organic and inorganic building blocks.<sup>1</sup> As an emerging class of nanoporous solids with modular nature,<sup>2</sup> MOFs exhibit predictable topology, tailorable porosity, and tunable functionality, and are suited for a wide range of applications including gas storage, catalysis, and sensing, to name a few.<sup>3</sup> To further broaden the utility of MOFs, it is important to increase the complexity and/or introduce synergistic effects without compromising their ordered structure.<sup>4</sup> One synthetic strategy is to introduce “heterogeneity within order”,<sup>5</sup> a concept developed by Yaghi and co-workers, who have demonstrated the facile incorporation of up to eight distinct linkers with similar length but different functionalities into one single framework.<sup>6</sup> Despite the lack of knowledge of the exact location of each functional group due to the disordered distribution within the framework, the resulted multivariate MOFs (MTV-MOFs) can exhibit enhanced properties in gas adsorption<sup>7</sup> and multifunctional heterogeneous catalysis<sup>8</sup> compared to their prototypic framework.

Another strategy to achieve a higher degree of functionality of MOFs is to place multiple topologically distinct linkers at the precise positions in the crystalline lattice, i.e., to construct MTV-MOFs with homogeneity. Although this objective can be achieved via a one-pot, mixed linker strategy where distinct linkers are simultaneously incorporated into one framework,<sup>9</sup> the postsynthetic stepwise ligand insertion<sup>10b</sup> appears to be a more reliable approach.<sup>10</sup> Recently, the Zhou group and the Su group utilizes the sequential linker installation (SLI) (or postsynthetic variable spacer installation, PVSI) to insert two different secondary linkers (SLs) in a stepwise fashion into a class of elastic PCN-700 (or LIFM-28) series.<sup>11</sup> Despite the

exciting progress, incorporating three distinct SLs within one framework remains a challenge and, to the best of our knowledge, has not been reported.

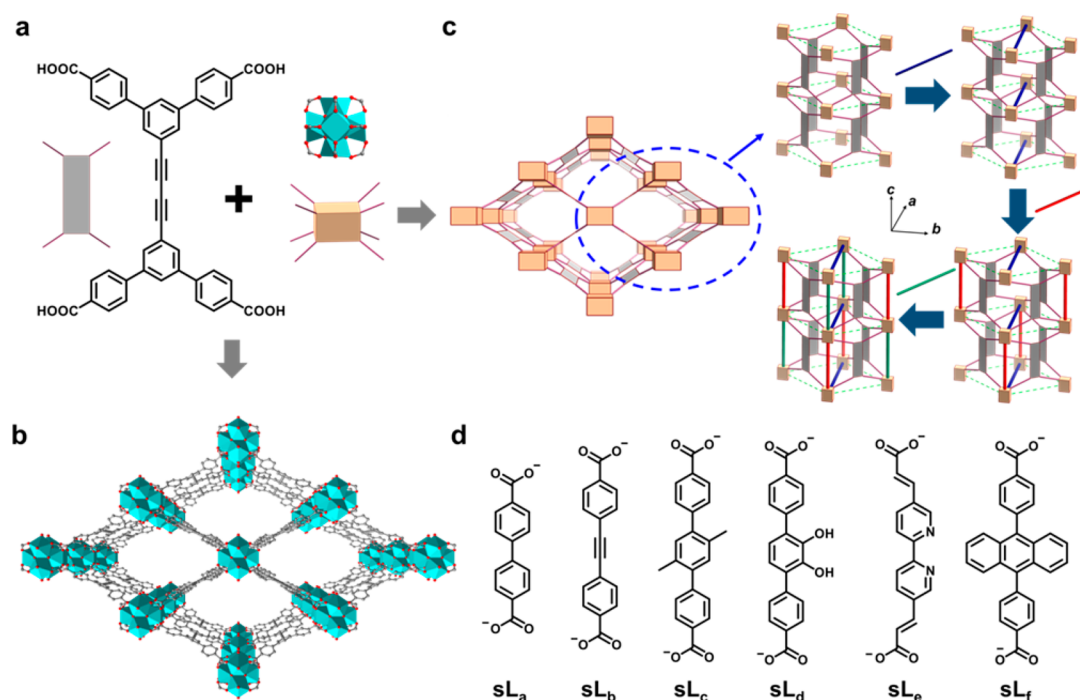
Herein, we disclose the construction of a new series of MTV-MOFs with homogeneity via a topology-guided stepwise insertion of three different SLs within a prototypic Zr-MOF (NPF-300, NPF = Nebraska Porous Framework) (Figure 1). Assembled from a planar tetratopic primary linker **L** and eight-connected  $\text{Zr}_6\text{O}_4(\text{OH})_8(\text{H}_2\text{O})_4$  clusters, NPF-300 exhibits the unique *scu* topology. Upon the removal of the  $\text{OH}^-/\text{H}_2\text{O}$  ligands of the  $\text{Zr}_6$  clusters, a secondary linear dicarboxylate linker with an appropriate length can be first inserted into the framework along the *a* axis (Figure 1c). Next, the in-plane and out-of-plane bending flexibility of the primary linker **L** enables the stepwise insertion of two other SLs along the *c* axis. Detailed stability evaluations reveal that the size-matching and the framework strain are two important factors that dictate the interplay between the thermodynamics and kinetics of the linker insertion and dissociation. Overall, this topology-guided secondary linker insertion enables the permanent porosity of NPF-300 and the potentials for the installation of multiple functionalities in a new prototype of MTV-MOFs.

## RESULTS AND DISCUSSION

Tetratopic ligand  $\text{H}_4\text{L}$  was synthesized via the typical Suzuki, Sonogashira, and Glaser coupling followed by saponification in basic aqueous solution (see Supporting Information, SI-2, for detailed procedure). Light-yellow crystals of NPF-300 were obtained via a solvothermal reaction of  $\text{ZrCl}_4$  with  $\text{H}_4\text{L}$  in dimethylformamide (DMF):dimethylacetamide (DEF) (v:v =

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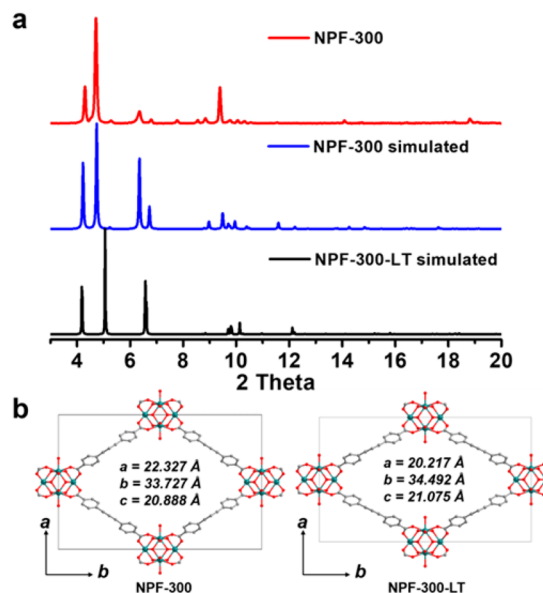
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**Figure 1.** (a) Primary tetratopic linker L and Zr<sub>6</sub> cluster, their topological representation (C, gray; O, red, Zr, cyan polyhedron). (b) Structure of NPF-300. (c) The augmented scu and schematic illustration of the stepwise insertion of three SLs. (d) Structure of the six SLs used in this study.

8:1) with benzoic acid as the modulating agent at 120 °C for 48 h. Single-crystal X-ray diffraction (sc-XRD) study at room temperature reveals that NPF-300 crystallizes in the orthorhombic crystal system with a *Cmmm* space group. Each tetratopic ligand L is connected to four Zr<sub>6</sub> clusters that are organized in a C-centered orthorhombic arrangement (Figure S16, SI). Each Zr<sub>6</sub> cluster is coordinated with eight L linkers with four above and four below the equatorial plane and eight terminal H<sub>2</sub>O/OH<sup>−</sup> groups in the equatorial plane (Figure S17), which gives the overall formula of NPF-300 as Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>8</sub>(H<sub>2</sub>O)<sub>4</sub>L<sub>2</sub>. The combination of the large size of linker L and the unique scu topology<sup>12</sup> results in four large 1D open channels in NPF-300, namely, rhombic channels of with a size of 27 × 15 Å along the *c* axis, rhombic channels with a size of 9 × 13 Å along the *b* axis, rhombic channels of with a size of 8 × 9 Å and hexagonal channels with a diameter of 15 Å along *a* axis (Figures S13–S15).

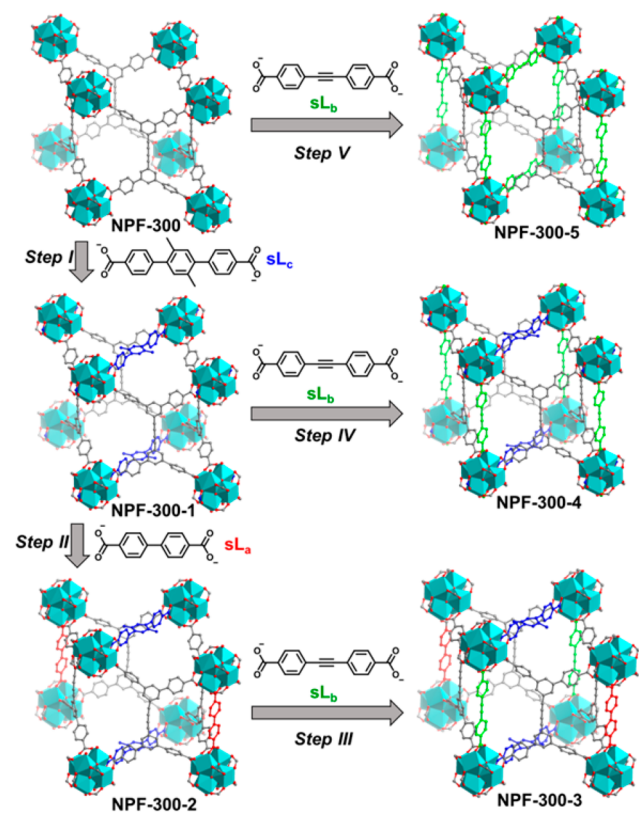
The powder XRD pattern of the solvated NPF-300 exhibits an excellent agreement with the simulation, confirms the bulk purity of the material (Figure 2a). Interestingly, a second sc-XRD study of NPF-300 at 110 K (designated as NPF-300-LT) reveals a 10% decrease of the crystallographic *a* axis and 2.2% and 1% increase of the *b* and *c* axes, respectively, as well as an overall 7.0% decrease of unit cell volume (Figure 2b, Table S1). A Hf-MOF (NPF-300(Hf)) also exhibits similar cell parameters at 110 K (Table S1). A close examination of the crystal structure shows that the temperature-dependent deformation is mainly due to the subtle change of the conformation of ligand L: the dihedral angle between the terminal and the center phenyl rings of L in NPF-300 and NPF-300-LT is 42.2° and 39.6°, respectively (Figure S18), which results in a small flexibility of NPF-300 crystals along the *a* axis. Zr-MOFs consisting 8-connected Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>8</sub>(H<sub>2</sub>O)<sub>4</sub> clusters are ideal platforms for SL insertion via the replacement of OH<sup>−</sup>/H<sub>2</sub>O groups on the clusters.<sup>11,13</sup> Encouraged by the small flexibility of NPF-300 along the *a* axis, we first tested the possibility to



**Figure 2.** (a) Experimental and simulated powder XRD patterns of NPF-300 and NPF-300-LT. (b) Structure of NPF-300 and NPF-300-LT viewed from the *c* axis.

insert linker SL<sub>c</sub> as the first SL since its length (15.4 Å) is close to the O–O distance between the adjacent Zr<sub>6</sub> clusters along the *a* axis (14.5 Å) (Scheme 1, Step I). Briefly, NPF-300 crystals were placed in the solution of SL<sub>c</sub> in DMF at 60 °C for 24 h, and the resulting crystalline material, termed as NPF-300–1, crystallizes in the same *Cmmm* space group as NPF-300 and displays the presence of SL<sub>c</sub> at the expected position. In NPF-300–1, each Zr<sub>6</sub> cluster is 10-connected to eight primary L and two secondary SL<sub>c</sub> linkers, with the overall composition of Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>6</sub>(H<sub>2</sub>O)<sub>2</sub>(L)<sub>2</sub>(SL<sub>c</sub>), which is confirmed by <sup>1</sup>H NMR of a digested sample (vide infra, Table 1 and Figure S5).

Scheme 1. Stepwise Insertion of SL in NPF-300



The powder XRD patterns reveal the crystallinity of the bulk material and confirm the nature of single-crystal-to-single-crystal transformation (Figure S21).

Upon the insertion of first SL  $sL_c$ , the O–O distance between the adjacent 10-connected  $Zr_6$  clusters along the  $c$  axis is 12.8 Å, close to the length of the linear ditopic linker  $sL_a$  (11.3 Å). We then used  $sL_a$  as the second SL for the insertion in NPF-300–1 using a similar method and successfully obtained the single crystals of NPF-300–2 (Scheme 1, Step II). NPF-300–2 crystallizes in the *Immm* space group, and its unit cell is nearly doubled compared to NPF-300 and NPF-300–1 due to the alternating arrangement of  $sL_a$  between the adjacent  $Zr_6$  clusters along the  $c$  axis. Thus, each  $Zr_6$  cluster is 11-connected to eight primary  $L$ , two  $sL_c$  and one  $sL_a$ , with the overall composition of  $Zr_6O_4(OH)_5(H_2O)(L)_2(sL_c)(sL_a)_{1/2}$ , which was confirmed by  $^1H$  NMR (vide infra, Table 1 and Figure S6).<sup>14</sup> Remarkably, the O–O distance between the adjacent 11-connected  $Zr_6$  clusters in NPF-300–2 along the  $c$  axis is 14.5 Å, suitable for the insertion of a third SL  $sL_b$  with a

length of 13.8 Å, which yielded NPF-300–3 (Scheme 1, Step III). The space group of NPF-300–3 remains as *Immm*, and each  $Zr_6$  cluster is now 12-connected to eight primary  $L$  and two  $sL_c$ , one  $sL_a$ , and one  $sL_b$  with the overall composition of  $Zr_6O_4(OH)_4(L)_2(sL_c)(sL_a)_{1/2}(sL_b)_{1/2}$ , which is confirmed by  $^1H$  NMR (vide infra, Table 1 and Figure S7). Powder XRD analysis also confirms the bulk crystallinity of NPF-300–2 and NPF-300–3 (Figures S22 and S23).

The successful stepwise insertion of three distinct SLs in NPF-300 benefits from the unique *scu* topology and relatively large size of the primary tetratopic ligand  $L$  that offers unique spaces to accommodate linker insertion. More importantly, the flexibility of the phenyl–alkynyl–alkynyl–phenyl backbone of the primary ligand plays an important role. A close comparison of molecular geometry of  $L$  in NPF-300–1 and NPF-300–2 reveals a small but critical out-of-plane and in-plane distortion, indicated by the change of the dihedral angle between two central phenyl planes from 0° to 11.1° and the change of symmetry from  $C_{2h}$  to  $C_s$  (Figure 3). Such distortion is caused by the half occupancy of  $sL_a$  within the empty space along the  $c$  axis and offers the possibility of the third SL insertion.

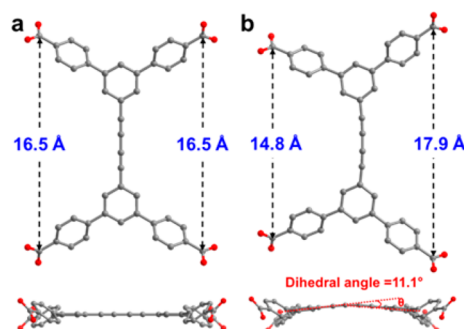


Figure 3. Top and side views of the conformation of primary linker  $L$  in NPF-300–1 (a) and NPF-300–2 (b) showing the in-plane and out-of-plane distortion.

It should be noted that the length of SL and the sequence of insertion is essential to a successful insertion.<sup>11a</sup> For instance, inserting a slightly longer linker  $sL_b$  instead of  $sL_a$  as the second SL into NPF-300–1 results in its complete occupancy along the  $c$  axis (Scheme 1, Step IV). The resulting single crystal material, termed as NPF-300–4, has a composition of  $Zr_6O_4(OH)_4(L)_2(sL_a)(sL_b)$ . Moreover, the attempted insertion of  $sL_b$  first along the  $c$  axis in NPF-300 was not successful and instead led to the simultaneous linker insertion along both  $a$  and  $c$  axes and yielded NPF-300–5, a framework with the overall composition of  $Zr_6O_4(OH)_4(L)_2(sL_b)_2$  (Scheme 1, Step

Table 1. Chemical Stability of NPF-300 MTV-MOFs

|           | molar ratio                 | theoretical value | as prepared <sup>a</sup>    | water <sup>a,b</sup>        | pH = 11 <sup>a,c</sup>      | pH = 1 <sup>a,d</sup>       |
|-----------|-----------------------------|-------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| NPF-300–1 | L: $sL_c$                   | 2:1               | 2.00:1.00                   | 2.00:1.00                   | 2.00:1.00                   | 2.00:1.04                   |
| NPF-300–2 | L: $sL_c$ : $sL_a$          | 2:1:0.5           | 2.00:1.10:0.92 <sup>e</sup> | 2.00:1.04:0.79 <sup>e</sup> | 2.00:1.07:0.76 <sup>e</sup> | 2.00:0.71:0.61 <sup>e</sup> |
| NPF-300–3 | L: $sL_c$ : $sL_a$ : $sL_b$ | 2:1:0.5:0.5       | 2.00:0.97:0.52:0.58         | 2.00:1.00:0.49:0.57         | 2.00:1.01:0.46:0.56         | 2.00:0.67:0.10:0.27         |
| NPF-300–4 | L: $sL_c$ : $sL_b$          | 2:1:1             | 2.00:1.04:1.05              | 2.00:1.04:0.98              | 2.00:1.03:0.93              | 2.00:0.16:0.43              |
| NPF-300–5 | L: $sL_b$                   | 2:2               | 2.00:1.99                   | 2.00:1.51                   | 2.00:1.16                   | 2.00:0.49                   |

<sup>a</sup>Molar ratios were calculated by comparing the characteristic peaks of samples digested in  $K_3PO_4$  solution in  $^1H$  NMR, as shown in Figures S41–S44. A standard deviation of 10% was estimated based on three measurements. <sup>b</sup>Samples soaked in water. <sup>c</sup>Samples soaked in solutions with pH values adjusted by HCl. <sup>d</sup>Samples soaked in solutions with pH values adjusted by NaOH. <sup>e</sup>The values are higher than the expected value (0.5), indicating the additional binding of  $sL_a$  along the  $c$  axis, most likely via one of the carboxyl groups.



Table 2. Porosity Parameters, Density, and N<sub>2</sub> Uptakes for NPF-300 MTV-MOFs

|                                                                  | NPF-300 | NPF-300-1 | NPF-300-2 | NPF-300-3 | NPF-300-4 | NPF-300-5 |
|------------------------------------------------------------------|---------|-----------|-----------|-----------|-----------|-----------|
| SA <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> ) <sup>a</sup> | 419     | 3276      | 2963      | 2750      | 2978      | 2565      |
| SA <sub>V</sub> (m <sup>2</sup> mL <sup>-1</sup> )               | 109     | 1657      | 1564      | 1529      | 1611      | 1449      |
| V <sub>p</sub> (cm <sup>3</sup> g <sup>-1</sup> )                | 0.26    | 1.63      | 1.18      | 1.11      | 1.19      | 1.03      |
| D <sub>c</sub> (g cm <sup>-3</sup> )                             | 0.456   | 0.512     | 0.528     | 0.556     | 0.541     | 0.565     |
| N <sub>2</sub> uptake <sup>c</sup>                               | 121     | 853       | 763       | 715       | 771       | 669       |

<sup>a</sup>Surface area (m<sup>2</sup> g<sup>-1</sup>) calculated from N<sub>2</sub> adsorption at 77 K based on the BET model. <sup>c</sup>One bar; unit of gas uptake, cm<sup>3</sup> g<sup>-1</sup>.

V). This is likely due to the intrinsic flexibility of NPF-300 for accommodation of sL<sub>b</sub> (13.8 Å) in all three positions. Similarly, <sup>1</sup>H NMR and powder XRD analysis confirmed the composition and bulk crystallinity. (Table 1 and Figures S24 and S25).

With the MTV-MOF materials in hand, we next assessed their thermal stability via thermogravimetric analysis. All MOFs exhibit a high decomposition temperature around 450–500 °C, indicating their good thermal stability at elevated temperature (Figure S49). Excellent crystallinity also remains after treatment in H<sub>2</sub>O, basic (pH = 11), and acidic (pH = 1) conditions (Figure S40). However, the chemical stability of NPF-300 series is better quantified by digestion analysis. This is because the partial or complete dissociation of SLs in MTV-MOFs does not necessarily result in a change of crystallinity. Indeed, upon digestion, <sup>1</sup>H NMR spectra revealed the dissociation of SLs to various extent. Using the primary ligand L as the internal reference, the relative molar ratio before and after the treatments was quantified and summarized in Table 1.

First, among the five MTV-MOFs, NPF-300-1 exhibits the highest stability as indicated by the consistent L:sL<sub>c</sub> molar ratio of ~2:1 in water, basic, and acidic conditions (Table 1). This can be attributed to the good size-matching of sL<sub>c</sub> and the distance between the adjacent Zr<sub>6</sub> clusters along the *a* axis. Such thermodynamic stability is also indicated by the insignificant change of powder XRD patterns (Figure S40) and unit cell volume (~0.4% increase) after the ligand insertion (Table S1). Second, the overall stability of other four MTV-MOFs follows the trend: water > pH = 11 > pH = 1. Except NPF-300-5, all MTV-MOFs exhibit impressive stability in water and basic conditions. At the same time, the chemical stability is roughly in correlation to the deviation of the lattice parameters from NPF-300-1. For instance, compared to NPF-300-1, the unit cell volume of NPF-300-4 and NPF-300-5 increases by 2.6% and decreases by 4.7%, respectively (Table S1). Accordingly, the inserted SLs in these two MOFs are more kinetically controlled and significantly dissociate especially in acidic solution (Table 1). Lastly, the dissociation of sL<sub>a</sub> and sL<sub>b</sub> also causes the simultaneous detachment of sL<sub>c</sub>. Specifically, in contrast to its high stability in NPF-300-1, sL<sub>c</sub> partially dissociates in NPF-300-2 and NPF-300-3 in acidic condition (e.g., L:sL<sub>c</sub> ratio decreases from 2.00:1.04 to 2.00:0.71 and 2.00:0.67, respectively).

Overall, in contrast to PCN-700 and LIFM-28 series where the dynamic twisting of the primary ligand plays an essential role in the insertion and water-promoted, facile dissociation of SLs,<sup>11d</sup> the ligand insertion in NPF-300 series is more based on size-matching, which exerts less mechanical strain on the primary framework and results in the significantly improved stability of NPF-300 series in aqueous solutions. In particular, with the insertion of a size-matched linker and the least amount of strain, NPF-300-1 exhibits excellent resistance toward acidic and basic conditions.

We next determined the porosity parameters of NPF-300 series. Unlike some other Zr-MOFs with scu topology, NPF-300 loses its crystallinity upon desolvation (Figure S20).<sup>12c,f-i,15</sup> Even after the activation by supercritical CO<sub>2</sub> exchange,<sup>16</sup> it only exhibits a low BET surface area (SA<sub>BET</sub>) of 419 m<sup>2</sup>/g (Table 2 and Figure S29). To our delight, the insertion of SLs enables the permanent porosity of all MTV-MOFs. In particular, NPF-300-1, with sL<sub>c</sub> inserted along the *a* axis exhibits the highest SA<sub>BET</sub> of 3236 m<sup>2</sup>/g, an increase more than seven times (Table 2 and Figure S30). The insertion additional linkers such as sL<sub>a</sub> (in NPF-300-2) and sL<sub>b</sub>+sL<sub>a</sub> (in NPF-300-3), albeit the retention of permanent porosity, however results in a slight decrease of SA<sub>BET</sub> due to their occupation of the free space inside the MOF cavity (Table 2 and Figures S31 and S32). Among the three MTV-MOFs with full insertion of SLs, NPF-300-4 exhibits the highest SA<sub>BET</sub> (2978 m<sup>2</sup>/g, 16.1% higher than NPF-300-5), which is correlated to its largest cell volume (7.7% larger than NPF-300-5) (Table 2 and Figures S33 and S34).

It should be pointed out that the regioselectivity for sL<sub>b</sub> insertion in forming NPF-300-5 is poor. It is observed that, as the amount of sL<sub>b</sub> used in the linker insertion in NPF-300-5 increases, the SA<sub>BET</sub> of the resulting material increases (Figure 4). Since the realization of surface area is closely related to the

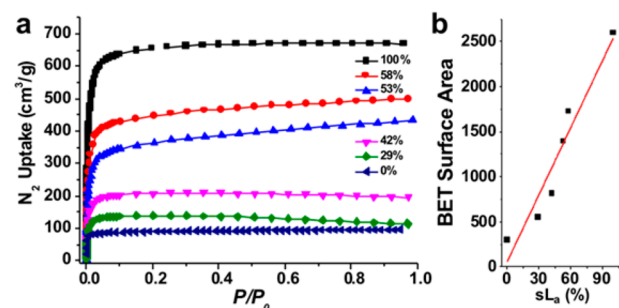


Figure 4. (a) N<sub>2</sub> gas adsorption isotherm and (b) SA<sub>BET</sub> for NPF-300 with different amount of inserted linker sL<sub>b</sub>. The percentage was calculated using the experimentally determined value vs the theoretical amount assuming complete insertion was obtained.

linker insertion along the *a* axis, the pseudo linear correlation between the SA<sub>BET</sub> and the ratio of inserted ligand (determined by <sup>1</sup>H NMR after digestion) strongly suggests that insertion along both *a* and *c* axis occurs simultaneously. In addition, powder XRD patterns also demonstrate the gradual change of unit cell parameters as the ligand insertion proceeds (Figure S38).

Having established their permanent porosity, we further tested the potential utility of NPF-300 series in gas storage by evaluating the uptake capacity for H<sub>2</sub>, CO<sub>2</sub>, and CH<sub>4</sub>. Thanks to their permanent porosity, all five MTV-MOFs exhibit significantly better performance compared to the collapsed

prototypic NPF-300 (Figures S46–S48, Table S2). In particular, NPF-300–1 shows the highest uptake for H<sub>2</sub> (1.7 wt % at 77 K), CO<sub>2</sub> (15 wt % at 273 K), and CH<sub>4</sub> (1.4 wt % at 273 K), due to its largest surface area, pore volume, and lowest density (Table 2). It is interesting that at low pressure (0–40 mmHg), the CO<sub>2</sub> adsorption of NPF-300–2 is the highest among all (Figure S48), which is likely due to the strong interaction between CO<sub>2</sub> and the extra dangling sL<sub>a</sub> we proposed to account for its high ratio. It is foreseeable that the current moderate performance can be readily improved via further functionalization of the secondary linkers such as sL<sub>c</sub> and sL<sub>a</sub> to achieve enhanced gas adsorption capability as well as selectivity.<sup>11b,e</sup> Other functional SLs with metal chelating group can also be incorporated in NPF-300. For example, we were able to insert catechol<sup>17</sup> and bipyridine-based<sup>18</sup> SLs (i.e., sL<sub>d</sub> and sL<sub>e</sub>) and obtained the corresponding NPF-300–6 and –7, respectively (Figures S10 and S11 and Table S1). The similar length of sL<sub>d</sub> and sL<sub>e</sub> to sL<sub>c</sub> enables insertion along the *a* axis as such in NPF-300–1. Similarly, sL<sub>f</sub>, a secondary linker derived from DPA (9,10-diphenylanthracene) can also be inserted and forming NPF-300–8 (Figure S12 and Table S1), which can be potentially utilized for heterogeneous photophysical and photochemical applications.<sup>19</sup>

In summary, we have synthesized a new class of prototypic MTV-MOFs based on the (4,8)-connected NPF-300 series using topology as a guidance. The unique positions of eight-connected Zr<sub>6</sub> clusters in the scu network and the flexibility of the tetratopic primary linker L enable the precise insertion of up to three different distinct secondary linkers along the *a* and *c* axis via stepwise, single-crystal-to-single-crystal transformation. We have revealed that the size-matching of the inserted linker and the framework strain are two important factors that govern the overall stability of MTV-MOFs. To the best of our knowledge, NPF-300 represents the first structure prototype that has the capability to introduce three distinct functional groups into a single MOF in a crystallographically ordered fashion. It is our expectation that NPF-300 can be used to build multifunctional MOF materials for a wide range of applications including gas storage/separation and synergistic/cooperative catalysis.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.8b04277.

Materials, general experimental procedures, synthesis of NPF-300 series, and characterizations of compounds (PDF)

Crystallographic data (CIF)

Crystallographic data (CIF)

Crystallographic data (CIF)

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### Notes

The authors declare no competing financial interest.

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