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# Fabrication of (4, 10) and (4, 12)-Connected Multifunctional Zirconium Metal–Organic Frameworks for the Targeted Adsorption of a Guest Molecule

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**S** Supporting Information

ABSTRACT: Following the principle of a topology guide, a zirconium MOF (PCN-207) based on the H<sub>4</sub>TPTA ligand (tetramethyl(4,4',4",4"'-(pyrazine-2,3,5,6-tetrayl))tetrabenzoic acid) with C2 symmetry and an 8-connected  $Zr_6(\mu_3$ -OH) $_8$ (OH) $_8$ ]<sup>8+</sup> cluster with  $D_{4h}$  symmetry has been synthesized. PCN-206 can also be obtained by modulating the benzoic acid usage to change the flexibility of the H<sub>4</sub>TPTA ligand. The unique positions of 8-connected Zr<sub>6</sub> clusters in the *flu* and *scu* networks and the flexibility of the tetratopic primary linker enable the precise insertion of fumarate (FA), 1,4-benzenedicarboxylic acid (H<sub>2</sub>BDC), and even 2,6-naphthalenedicarboxylic acid (H<sub>2</sub>NDC) in a one-pot reaction.



Auxiliary linkers are used to generate new MOF structures or topologies or to split the pore spaces, which may significantly change the porosity and chemical and physical properties of scaffold MOFs. The results provide a successful strategy for the rational design of multicomponent Zr-MOFs. Because of differences in composition and configuration between structures, PCN-207 shows the highest separation capability of light hydrocarbons; moreover, PCN-206 exhibits the highest adsorption capacity of 2,4-D and DCF among MOFs at present.

# INTRODUCTION

As a kind of highly porous and ordered crystalline material, metal organic frameworks (MOFs), linked by inorganic metal ions/clusters and organic linkers,<sup>1-4</sup> have proven potential applications in the fields of gas adsorption and separation,<sup>5,6</sup> light harvesting,<sup>7,8</sup> and catalysis.<sup>9,10</sup> In the past two decades, the development of coordination chemistry has overcome the drawbacks of traditional MOFs for practical applications, such as thermal and chemical stability.<sup>11</sup> According to the soft-hard acid-base theory, organic carboxylate MOFs with a high oxidation state ion or cluster show stronger coordination stabilities than transition element- or rare earth element-based MOFs.<sup>12–17</sup> Since Lillerud reported the first zirconium MOF, named UiO-66 with a  $[Zr_6O_4(OH)_4(BDC)_6]$  cluster, in 2008,<sup>18</sup> more and more scientific interest has focused on Zrbased MOFs because of their unparalleled thermal and chemical stability.

Among all reported Zr-MOFs, the Zr<sub>6</sub> cluster shows 6, 8, and 12 connections and in rare cases can be 9 and 10

connected.<sup>19-21</sup> Therefore, cluster flexibility makes topology predictions challenging for Zr-MOFs such as PCN-221-225,<sup>22-26</sup> MOF-801-841,<sup>21</sup> MOF-525-545,<sup>27</sup> and NU-1000-1200.<sup>28-30</sup> It should be noted that the introduction of flexible ligands makes topology predictions more complex. It is a great challenge to design and target the topologies of Zr-MOFs when we take the linker complexity and cluster flexibility into consideration at the same time. A recent report by Matzger has discussed the effects of linker geometry and flexibility on the formation of different Zr-tetratopic carboxylate MOFs.<sup>31</sup> They demonstrated that Zr-MOFs with csq topology can be targeted by designing rectangularly shaped linkers with high aspect ratios. However, the shapes and aspect ratios of linkers are almost identical in csq- and scu-type frameworks. Very recently, Zhou and co-worker reported how to control the structure of

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Zr-tetracarboxylate frameworks through steric tuning and studied their formation mechanism intensively.  $^{\rm 32}$ 

With regard to multicomponent and mixed-linker MOFs, it is exceedingly difficult to control the structures and phase purity of the products in a one-pot reaction as a result of the increasing number of constituents and the appearance of multiple phases. Zhou's group recently developed a sequential linker installation strategy to map the exact position of a linker in a multicomponent MOF.<sup>33</sup> Moreover, considering that crystallization is an exclusionary rather than inclusionary phenomenon, our group succeeded in sieving and functionalizing Zr-MOFs with targeted structures using auxiliary linkers in a rigid ligand system by controlling the thermodynamic processes.<sup>34</sup>

Because of the development of coordination chemistry and reticular chemistry, the rational design and construction of MOFs with intricate structural complexity have been developed and have achieved great success. Thus, a pore space partitions (PSP) strategy was applied in tuning host–guest interactions.<sup>35</sup> For example, it can significantly enhance the framework stability and impact the gas sorption properties. As a result, pore environments of parent MOFs can be precisely controlled by introducing multiple components into MOFs, which contributes to synergetic gas storage and cooperative catalysis functions.

Herein, by modulating the thermodynamics using auxiliary linkers, we synthesized PCN-207 and PCN-206 with (4, 8)connected *flu* and *scu* topology, and after incorporating linear ligands, the structure of PCN-206 turned into a (4, 10)connected net and the structure of PCN-207 turned into a (4, 10)connected *zln* topology and (4, 12)-connected PCN-208. The introduction of auxiliary linkers can modulate the phase purity on a wider 2D scale together with new structures and topologies. A DFT calculation on the ligand energy barrier was used to interpret the formation of a PCN series. Besides, the adsorption and separation properties of PCN-206-208 before and after incorporating linear ligands have been investigated comparably, including the adsorption removal of pharmaceutical waste from water and the adsorption and separation of light hydrocarbons.

# RESULTS AND DISCUSSION

Structure Description of PCN-207. The solvothermal reaction of H<sub>4</sub>TPTA with zirconium tetrachloride and benzoic acid in DMF at 120 °C for 24 h led to the formation of colorless octahedral single crystals of PCN-207. X-ray singlecrystal diffraction indicates that PCN-207 crystallizes in orthogonal space group Fmmm and contains 8-connected  $[Zr_6(\mu_3-OH)_8(OH)_8]^{8+}$  clusters connected by tetrahedral TPTA ligands (Figure 1a). All of the triangular faces in each  $[Zr_6(\mu_3-OH)_8(OH)_8]^{8+}$  cluster are capped with  $\mu_3$ -OH groups. Only eight edges are linked by carboxylates from tetrahedral TPTA<sup>4-</sup> ligands, which is different from that of the UiO series, and the remaining coordination sites are terminal -OH/H<sub>2</sub>O groups. To satisfy the demands of symmetry, both  $Zr_6(\mu_3$ -OH)<sub>8</sub>(OH)<sub>8</sub>]<sup>8+</sup> clusters and tetrahedral TPTA<sup>4-</sup> ligands suffer a symmetry reduction. The symmetry of  $[Zr_6(\mu_3 - OH)_8(OH)_8]^{8+}$  clusters in PCN-207 has changed from  $O_h$  to  $D_{4h}$ , which has been reported in PCN-222,<sup>23</sup> PCN-521,<sup>32</sup> and MOF-545.<sup>27</sup> At the same time, the symmetry of the tetrahedral TPTA ligands is also reduced to the lowest  $C_2$  with the angles of two adjacent phenyl rings at about 66.05 and 115.12°, which



**Figure 1.** (a) Structure of  $H_4$ TPTA. (b) 8-Connected  $Zr_6$  cluster in PCN-207. (c) Dodecahedral cage in the framework of PCN-207. (d) Augmented *flu* topology of PCN-207, where the purple and turquiose polyhedra represent 4- and 8-connected nodes, respectively.

is different from the  $109^{\circ}28'$  in an ideal tetrahedron (Figure 1b).

Moreover, in the structure of PCN-207, each  $[Zr_6(\mu_3 -$ OH)8(OH)8]<sup>8+</sup> SBU is surrounded by eight tetrahedral TPTA<sup>4-</sup> ligands, and each TPTA<sup>4-</sup> links four  $[Zr_6(\mu_3 OH)_{8}(OH)_{8}^{8+}$  SBUs. Thus, there is a kind of open dodecahedral cage in the framework of PCN-207 with dimensions of about 27.06  $\times$  24.35  $\times$  10.33 Å<sup>3</sup>, with three hanging open windows in sizes of  $12.73 \times 13.59$ ,  $11.93 \times 9.92$ , and 14.9  $\times$  6.65 Å<sup>2</sup>, respectively, consisting of eight TPTA<sup>4-</sup> tetrahedra and six  $[Zr_6(\mu_3-OH)_8(OH)_8]^{8+}$  SBUs as vertices and 24 TPTA<sup>4-</sup> ligand edges (Figure 1c). These dodecahedral cages are further connected into a 3D open framework by sharing their rhombic facets. From the viewpoint of topology, the  $[Zr_6(\mu_3\text{-}OH)_8(OH)_8]^{8+}$  SBUs can be viewed as eight connected nodes and tetrahedral TPTA<sup>4-</sup> ligands can be regarded as four connected linkers. Hence, the tetrahedral  $TPTA^{4-}$  ligands link  $[Zr_6(\mu_3-OH)_8(OH)_8]^{8+}$  SBUs to form a (4, 8)-connected net with *flu* topology, which has been shown in two reported rigid Zr-MOFs (PCN-521<sup>32</sup> and MOF-841<sup>21</sup>) based on similar inorganic  $[Zr_6(\mu_3-OH)_8(OH)_8]^{8+}$  units connected by organic ligands (Figure 1d).

Effect of Benzoic Acid in a One-Pot Reaction. As we all know, the modulating linkers will affect the coordination of linkers and/or clusters, which will impact the final structure and the phase purity. For example, PCN-222 and PCN-224 can be sieved and purified to some degree by tuning the concentration of benzoic acid. When we decrease the concentration of BA from 1.85 to 1.1 M, a PCN-206 powder is obtained. Powder X-ray diffraction analysis indicates that PCN-206 crystallizes in orthogonal space group Cmmm and contains 8-connected  $[Zr_6(\mu_3-OH)_8(OH)_8]^{8+}$  clusters and 4connected TPTA<sup>4-</sup> ligands (Figure 2a). TPTA<sup>4-</sup> ligands adopt a rectangular planar conformation with  $C_{2h}$  symmetry, which is different from tetrahedral in PCN-207. As shown in Figure 2b,  $[Zr_6(\mu_3-OH)_8(OH)_8]^{8+}$  clusters with  $D_{4h}$  symmetry were connected by TPTA<sup>4-</sup> ligands, which is similar to that of PCN-207, creating a porous framework with rhombic channels



**Figure 2.** (a) Structure of  $H_4$ TPTA. (b) 8-Connected  $Zr_6$  cluster in PCN-206. (c) Dodecahedral cage in the framework of PCN-206. (d) Augmented *scu* topology of PCN-206, where the purple and turquiose polyhedra represent 4- and 8-connected nodes, respectively.

that are approximately  $15.2373 \times 26.775 \text{ Å}^2$  in diameter in the *c* axis (Figure 2c). The walls of the rhombic channel are composed of two channels with diameters of  $14.44 \times 11.35$  and  $14.32 \times 8.4 \text{ Å}^2$  in an axis. Therefore, PCN-206 adopts a (4, 8)-connected network with *scu* topology (Figure 2d).

Effect of Second Modulating Linkers in a One-Pot Reaction. A careful inspection of the structure of PCN-206 and PCN-207 shows that each cluster is connected by eight carboxylate groups with the remaining four coordination sites occupied by aqua ligands. Two of them are in the equatorial plane, and the distance between two adjacent  $Zr_6$  clusters is 5.0 and 6.262 Å, which can accommodate a linear dicarboxylate linker by replacing the terminal OH<sup>-</sup>/H<sub>2</sub>O via an acid–base reaction, such as with fumarate (FA), 1,4-benzenedicarboxylic acid (H<sub>2</sub>BDC), and 2,6-naphthalenedicarboxylic acid (H<sub>2</sub>NDC). Considering the similar length between second modulating linkers and two adjacent  $Zr_6$  clusters, the one-pot method was applied. Fortunately, FA can be accommodated into PCN-206, and H<sub>2</sub>BDC and H<sub>2</sub>NDC ligands are installed into the pocket of PCN-207. PCN-207 exhibits excellent spongelike behavior, which contributes to the flexible of H<sub>4</sub>TPTA ligands on the *a* axis. The resulting compounds, designated as PCN-206-FA, PCN-207-BDC, and PCN-207-NDC, maintain adequate crystallinity following guest encapsulation and are subsequently analyzed by single-crystal X-ray diffraction and PXRD. The existence and positions of BDC and NDC are unambiguously observed in the crystallo-graphically resolved structure (Figure 3).

As for PCN-207-BDC and PCN-207-NDC, both of them crystallize in the Fmmm space group. Interestingly, the unit cells of PCN-207-BDC and PCN-207-NDC gradual changed in size compared to the prototype MOF (PCN-207). A significant increase in the length of the a axis (from 14.1 to 16.5 Å) and a slight decrease in the length of the b/c axis were observed upon linker inclusion. Tetrahedral TPTA<sup>4-</sup> ligands also adopt the lowest  $D_2$  symmetry, with the angles of two adjacent phenyl rings being about 67.48 and 114.39° for PCN-207-BDC and 35.89 and 53.73° for PCN-207-NDC. With regard to PCN-206-FA, it also adopts the *Cmmm* space group. There is no obvious change between PCN-206 and PCN-206-FA in the unit cell parameter because of the perfect match in length between the pockets and FA linkers. The crystallographic data for PCN-206, PCN-206-FA, PCN-207, and PCN-207-BDC are summarized in Table S1. Take PCN-207-BDC as an example: each Zr<sub>6</sub> cluster is 10-connected to 8 TPTA<sup>4-</sup> and 2 BDC linkers. It is very interesting that the dodecahedral cage observed in the framework of PCN-207 was divided into two half-dodecahedral cages. The topology of PCN-206-FA, PCN-



Figure 3. Structures of different MOF pairs with pockets to selectively accommodate different auxiliary linkers: PCN-206 for FA, PCN-207 for BDC, and PCN-208 for NDC.



Figure 4. Topologies for (a) PCN-206-FA, (b) PCN-207-NDC, and (c) PCN-208-NDC.



Figure 5. Synthesis map showing the effect of auxiliary linkers. (a) PCN-206 and PCN-207 modulated by FA and (b) PCN-206, PCN-207, and PCN-208 modulated by NDC.

207-BDC, and PCN-207-NDC changed from a (4, 8)-connected net to a (4, 10)-connected net.

What is more interesting is that PCN-208-NDC can be obtained by incorporating more H<sub>2</sub>NDC linkers. It should be pointed out that PCN-208 could not be accessed directly under the present experimental conditions. The connected numbers of the PCN-207 and PCN-208 series vary from unsaturated (4, 8)- and (4, 10)- to saturated (4, 12)-connected after increasing the concentration of linear ligands gradually (Figure 4). Compared with the rotation of benzene rings in PCN-206 by 61.07° in the opposite direction, the benzene rings of PCN-208-NDC rotate 49.95° in the same direction, thus forming the new topological configurations. In PCN-208-NDC, each  $[Zr_6(\mu_3-O)_4(\mu_3-OH)_4]^{12+}$  linked eight TPTA<sup>4-</sup> and four NDC, and each TPTA<sup>4-</sup> is connected to four clusters to form (4,12)-c. The 8.17 × 16.38 Å<sup>2</sup> quadrilateral tunnels are divided into two different triangular tunnels by the NDC ligand, which are 6.64 × 8.16 and 10.49 × 8.16 Å<sup>2</sup>, respectively. Thus, <sup>1</sup>H NMR digestion experiments of digested PCN-206-FA, PCN-207-BDC, PCN-207-NDC, and PCN-208-NDC certify the different linker ratios in the synthesized MOFs, and they are formulated as  $[Zr_6(\mu_3-O)_4(\mu_3-OH)_4]$ - $[(OH)_2(H_2O)_2]TPTA_2FA$  (PCN-206-FA),  $[Zr_6(\mu_3-O)_4(\mu_3-OH)_4]$ [ $(OH)_{2.6}(H_2O)_{2.6}]TPTA_2NDC_{0.7}$  (PCN-207-NDC), and  $[Zr_6(\mu_3-O)_4(\mu_3-OH)_4][(OH)_{1.2}(H_2O)_{1.2}]TPTA_2NDC_{1.4}$  (PCN-208-NDC). Generally, the auxiliary linker contents in MOFs gradually escalate as their ratios in the starting materials increase, suggesting the partial occupation of auxiliary linkers.

Inspired by the success of Yaghi's group on multivariate MOFs, we also tried to use N<sub>3</sub>-BDC, NH<sub>2</sub>-BDC, OH-BDC, SO<sub>3</sub>Na-BDC, NO<sub>2</sub>-BDC, and 2,5-(OH)<sub>2</sub>-BDC linkers to exchange the H<sub>2</sub>BDC ligand in PCN-207-BDC in one-pot and linker exchange reactions,<sup>36</sup> but we failed to get any of them. There are mainly three reasons for this. First, because of

the steric hindrance between the pore and organic ligands, the pockets of PCN-207-BDC are not compatible for the BDC ligands with different functional groups. Second, the linker basicity ( $pK_a$ ) may be not suitable for substitution. Third, H<sub>2</sub>BDC ligands resist exchange, which indicates the stronger coordination capability between carboxylate and  $Zr_6$  clusters.

Synthesis Map Analysis in a One-Pot Reaction. Huge filtered experiments were carried out to systematically investigate the effect of second modulating linkers by fixing the concentration of benzoic acid and altering the linker ratios of the starting materials (Table S2). The effects of the linker ratio and modulating reagent are summarized in the synthesis map (Figure 5). PCN-206 can be obtained under a wide range of synthesis conditions by adding FA (Figure 5a). The use of BDC and NDC will promote the formation of PCN-207-BDC, PCN-207-NDC, and PCN-208-NDC, respectively. However, PCN-207 has one pocket to fit NDC and PCN-208 has two pockets per Zr<sub>6</sub> cluster. Therefore, the formation of PCN-207-NDC and PCN-208-NDC can be dictated by the amount of NDC added (Figure 5b). To form pure-phase PCN-207-NDC, the NDC concentration can be as high as 16 M to avoid the formation of PCN-208. Further increasing the NDC concentration favors the formation of PCN-208, which has more NDC in its structure. These phenomena are in line with Le Chatelier's principle. Normally, DUT-53 is thus formed if a large excess of NDC is added because of the potential competition between the primary linker and the auxiliary linker, but this situation can be avoided to a great extent because the tetratopic linkers are more competitive than the ditopic auxiliary linker.<sup>20</sup>

**DFT Calculation of the Ligand Energy Barrier.** To investigate the relationship between energy and structure, density functional theory (DFT) calculations were performed on the basis of M06-2X-D3/6-311G(d) using the *Gaussian 09* D.01 software package.<sup>37</sup> We calculated the single-point energy of each linker in the three compounds. Because all of the linkers in PCN-206, PCN-207, and simulated PCN-208 share the same composition and similar (4,8)-connected  $Zr_6$  clusters, the energy difference between each set of linkers is attributed to the structural differences. For comparison, all of the energy is normalized by subtracting the energy value of PCN-207. The relative energies of PCN-206 and PCN-208 are +32.197 and +56.839 kcal/mol, so the stable order of linkers is PCN-207 > PCN-206 > PCN-208, which matches very well with the experimental findings (Figure S2).

The permanent porosity of the PCN-206, -207, and -208 series has been confirmed with the as-synthesized sample by nitrogen sorption experiments at 77 K (Figure 6). PCN-206 and PCN-207 exhibit a type-I isotherm of N<sub>2</sub> sorption at 77 K and 1 bar, implying the existence of micropores in their structures. The N<sub>2</sub> uptake of PCN-207 is a little larger than that of PCN-206, and the Brunauer-Emmett-Teller (BET) surface areas of PCN-206 and PCN-207 are 1156 and 1241 m<sup>2</sup>  $g^{-1}$ , respectively. Nitrogen physisorption experiments on PCN-206-FA, PCN-207-BDC, PCN-207-NDC, and PCN-208-NDC at 77 K and 1 bar also revealed type-I isotherms with a maximum nitrogen uptake of 433 cm<sup>3</sup> g<sup>-1</sup> for PCN-206-FA, 354 cm<sup>3</sup> g<sup>-1</sup> for PCN-207-BDC, 323 cm<sup>3</sup> g<sup>-1</sup> for PCN-207-NDC, and 309 cm<sup>3</sup> g<sup>-1</sup> for PCN-208-NDC. The BET surface areas of PCN-206-FA, PCN-207-BDC, PCN-207-NDC, and PCN-208-NDC are 1428, 1194, 1107, and 1068 m<sup>2</sup> g<sup>-1</sup>, respectively, which is in good agreement with the single-crystal X-ray diffraction data. The permanent porosity is well



Figure 6.  $N_2$  sorption isotherms of PCN-206-208 systems at 77 K and 1 bar.

maintained before and after inserting the second linkers. The decrease in the BET surface areas of PCN-207-BDC, PCN-207-NDC, and PCN-208-NDC is a result of their occupation of the free space inside the MOF cavity. Surprisingly, the increase in the BET surface area of PCN-206-FA may contribute to the structurally rigid enhancement. To our delight, the pockets of PCN-207 and PCN-208 can be divided into two pieces. The insertion of FA, BDC, and NDC will affect the properties of PCN-207 and PCN-208 significantly, such as the changes in the pore environment, Lewis acid sites, the flexiblity and rigidity of the framework, the pore size distribution, and the thermal and chemical stabilities.

Thermal and Chemical Stability Analyses. To investigate the differences in the PCN-206-208 series, thermogravimetric analyses were performed to assess their thermal stability. As shown in Figure S3, PCN-206-208 is stable up to 400 °C and shows excellent thermal stability toward heat. Thus, the inset of the second linkers did not improve the thermal stability significantly, which also indicates the stability of the parent MOF. Take PCN-206-FA as an example. The inset of FA brings about an enrichment in rigidity but shows a small enhancement in thermal stability compared to that of PCN-206. It may contribute to the similar sizes between the pockets and FA linkers, melting point, and linker contents. A similar situation can be found in PCN-207-BDC. However, PCN-208-NDC has weak thermal stability, which is attributed to the ligand energy barrier. It also certifies that the energy value of PCN-207 is the lowest. We note that the influencing factors of the energy level of the ligand in the crystal cannot be evaluated solely by the distortion of linkers. It is possible that the insertion of the ancillary ligand affects the energy of the ligand, but from the results of the test, the insertion of the ancillary ligands slightly increases the stability of the corresponding series but does not cause large differences among the different series.

The chemical stabilities were first qualitatively analyzed by their PXRD patterns after treatment in acidic (pH 2), neutral (pH 7), and basic (pH 10 and 12) environments for 24 h (Figure S4). According to the results of PXRD, all of the samples had excellent crystallinity after treatment with acid and base, indicative of their superb chemical stabilities. Furthermore, take PCN-206-FA and PCN-207-BDC as examples. Their chemical stabilities are measured via quantified digestion



Figure 7. (a-c) Comparison of the adsorption effect at different pH values and (d-f) adsorption kinetics curves. PCN-206 (black), PCN-206-FA (red), PCN-207 (green), PCN-207-BDC (magenta), and PCN-208-NDC (navy).

analysis because of the high tolerance of defects in Zr-MOFs. Together with the results of <sup>1</sup>H NMR and PXRD, despite the partial or complete dissociation of FA and BDC ligands in acidic and basic environments, the resultant MOFs retain intact frameworks without a loss of crystallinity (Figures S5– S12).

**Removal of Pharmaceutical Wastewater.** The excellent thermal and chemical stabilities prompt us to investigate their practical applications. Covering drugs, cosmetics, and toiletries, these are collectively referred as pharmaceuticals and personal care products (PPCPs). Today's waste disposal is a more and more difficult task, especially for the treatment and utilization of water resources. These PPCPs have already pose a serious threat to water quality. However, the adsorption removal efficiency of conventional adsorbents, such as activated carbon, activated alumina and clay minerals, is usually very low.<sup>38,39</sup> Therefore, the efficient and selective removal of PPCPs from wastewater is extremely important and challenging.

In this work, the PCN-206, -207, -208 series was employed as PPCPs adsorbents to study the effect of different structural environments of MOF on PPCPs adsorption, explore their adsorption kinetics and structural function relationships, and provide a reference value for designing more efficient PPCP adsorbents. 2,4-Dichlorophenoxyacetic acid (2,4-D), clofibric acid (CLA), and diclofenac sodium (DCF) are three typical PPCPs<sup>40–42</sup> with water solubility that are often involved in life and are used as adsorption objects: 2,4-D with a molecular size of 10 × 5.6 × 1.8 Å<sup>3</sup> is listed by the international agency for research on cancer because of its toxicity and mutagenicity. CLA is a widely used herbicide with a molecular size of 10 × 5.0 × 4.3 Å<sup>3</sup>. DCF is one of the nonsteroidal anti-inflammatory drugs, and its molecular size is 9.3 × 7.4 × 1.8 Å<sup>3</sup>.

The excellent acid—base water stability of the PCN-206-208 series is necessary for the application of wastewater treatment. In view of this, the effect of water pH on adsorption was first explored. We placed 3 mg of Zr-MOF in 10 mL of a PPCP

aqueous solution with different pH values (pH 3, 5, 6 7, 9). Note that DCF is difficult to accommodate in solution with pH < 5 (PPCP concentration, 100 mg/L 2,4-D; 50 mg/L CLA and DCF, respectively). UV-vis spectroscopy was used to record changes in PPCP solution concentration (Figures \$13-\$18). PCN-206 and PCN-206-FA show good adsorption capacity for 2,4-D and DCF, and PCN-206-208 displays low adsorption to CLA. Nitrogen adsorption tests showed that PPCPs entered the pores of the MOF (Figure S19). For example, after PCN-206 adsorbs 2,4-D, DCF, and CLA, its N<sub>2</sub> adsorption decreases from 337.23 to 99.37, 81.61, and 272.89 cm<sup>3</sup>/g, respectively, and BET decreases from 1156 to 301.26, 289.57, and 642.35  $m^2/g$ , respectively. SEM images show that MOFs have no distinct changes in morphological after the adsorption of PPCPs (Figure S20). PXRD diffraction shows that the crystals maintain good crystallinity after the adsorption of PPCPs (Figure S21). PPCP adsorption results indicate that the pH value of the solution has little effect on the adsorption of PPCPs by MOFs (Figure 7a-c), which makes it more accessible and practical under the harsh conditions of wastewater. The adsorption capacity for 2,4-D and DCF with similar trends in loading amount is the following: PCN-206 > PCN-206-FA > PCN-208 > PCN-207 > PCN-207-BDC. The reasons for the different capture capabilities of the PCN-206-208 series may be as follows. First, the porosity of MOF is a prerequisite for the capture of macromolecular objects. Because the PCN-207 series belong to the flu configuration, the twist of the ligand forms the cage configuration, and the theoretical size of the open window ( $\sim 10 \times 12 \text{ Å}^2$ ) is similar to the three molecular sizes and even smaller in some directions  $(\sim 6 \times 14 \text{ Å}^2)$ . Therefore, PPCP cannot enter the oblate hole of PCN-207 to achieve capture. When BDC is inserted into PCN-207 to divide the cage, it is more difficult to achieve macromolecular capture. In PCN-208-NDC, the channels in PCN-208-NDC are also relatively small with 7.67  $\times$  8.16 Å<sup>2</sup> and  $10.49 \times 8.16$  Å<sup>2</sup> diameters, respectively, but it is beneficial to the entry of molecules compared to the cage structure. In contrast, the PCN-206 series possess unobstructed channels with 15.24  $\times$  26.78 Å<sup>2</sup> diameters in *scu* topology, and PPCP molecules are easier to access. On the other hand, we propose that the adsorption site of PPCP with MOF is -COOH, and the two adjacent methyl groups in CLA reduce the binding ability of CLA to MOF, resulting in the inability of MOF to capture CLA. The nitrogen atom in MOF is more likely to touch the binding -COOH site, interacting with carboxyl groups to capture PPCP. Furthermore, near-plane 2,4-D and DCF easily interact with the flat ligand on the PCN-206 channel walls. The above factors lead to the result that the adsorption capacity of the PCN-206 series for 2,4-D and DCF is much higher than for other series.

The adsorption kinetics of three PPCP molecules were simulated using pseudo-second-order kinetics with this model (r > 0.996) as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{1}{q_e} t$$
(1)

 $q_{\rm e}$  is the maximum adsorption amount of PPCPs at adsorption equilibrium (mg/g),  $q_t$  is the amount of adsorption at time t (h), and  $k_2$  is the pseudo-second-order rate constant (g mg<sup>-1</sup> h<sup>-1</sup>).

Subsequently, on the basis of the experimental data (Figure 7d-f), the pseudo-second-order kinetic parameters ( $k_2$  values)

of three different PPCP molecules were calculated by using eq 1 to plot the reticle ( $t/q_t$  versus t) (Figure S22, Table S4). The larger the  $k_2$  value, the faster the MOF adsorbs PPCP molecules. As shown in Table S4, for 2,4-D, the  $k_2$  value follows the order PCN-207  $\approx$  PCN-207-BDC > PCN-206 > PCN-208-NDC > PCN-206-FA, and the trends in the calculated  $k_2$  values of PPCPs@Zr-MOF composites are consistent with the experimental adsorption data. When the adsorption capacity is extremely small, the adsorption quickly reaches equilibrium, and when the adsorbed amount increases, the adsorption speed is also affected, which requires a relatively long time.

The study of adsorption kinetics and the initial adsorption capacity show that 2,4-D and DCF may be captured by MOFs in large quantities. We then further evaluated the adsorption capacity of different MOFs toward 2,4-D and DCF. MOFs of 0.30 mg/mL were added to a series of concentrations (ranging from 20 to 300 mg/L) of PPCPs, and then we used the Langmuir model to evaluate the MOFs' affinities for guest molecules. The Langmuir isotherm equation is given as

$$\frac{c_{\rm e}}{q_{\rm e}} = \frac{c_{\rm e}}{q_{\rm max}} + \frac{1}{q_{\rm max}}b \tag{2}$$

 $q_{\rm max}$  is the theoretical maximum adsorption capacity (mg/g),  $c_{\rm e}$  is the saturation/equilibrium concentration of PPCP in the supernatant (mg/L), and *b* is the Langmuir constant (related to the adsorption strength or affinity, L/mg).

The  $q_{max}$  values were then calculated and summarized according to the adsorption isotherms  $\frac{c_e}{q_e}$  (2) of Zr-MOF@ PPCPs in Figure S23 and are shown in Figure S24 and Table S5. We found that the PCN-206 series has obvious capture advantages for 2,4-D and DCF. The order of maximum adsorption capacity of 2,4-D/DCF is PCN-206 > PCN-206-FA > PCN-208-NDC > PCN-207 > PCN-207-BDC, and Langmuir constants are also in this order. PCN-206 has the largest adsorption capacity (470 mg/g for 2,4-D@PCN-206, 490 mg/g for DCF@PCN-206) and Langmuir constant (41.7 for 2,4-D@PCN-206, 76.3 for DCF@PCN-206). Because of the flat scu topology of PCN-206, it is more conducive to the entry of PPCP. PCN-206 and PCN-206-FA have capture capacities of 470 and 450 mg/g for 2,4-D and 490 and 210 mg/g for DCF, respectively. Regardless of the PCN-206-FA's ability to capture DCF, the adsorption capacity of PCN-206 for 2,4-D and DCF is currently the largest in the open literature. In addition, the insertion of FA slightly reduces the adsorption of 2,4-D, but limits the amount of DCF adsorption to half. Because the carbon-carbon double bond in FA has a high electron cloud density, it is mutually exclusive with  $-COO^{-}$  in DCF, inhibiting the entry of DCF. Compared to the traditional adsorbent activated carbon, the adsorption capacity is much greater and double that of other MOFs as well.<sup>26</sup> In contrast, the PCN-207 series has an adsorption capacity of only about 50 mg/g and PCN-208-NDC has capacities of 160 and 120 mg/g for 2,4-D and DCF, respectively. It can be seen that the distortion of the structure will cause the difference in the ability to adsorb guest molecules.

Adsorption and Separation of Light Hydrocarbons. Finally, we further tested the potential utility of the PCN-206, -207, and -208 series in gas storage and separation by evaluating single-component gas sorption isotherms for various light hydrocarbons ( $CH_4$ ,  $C_2H_2$ ,  $C_2H_4$ ,  $C_2H_6$ , and  $C_3H_6$ ) at



Figure 8. Sorption isotherms of hydrocarbons for desolvated (a) PCN-206, (b) PCN-206-FA, (c) PCN-207, (d) PCN-207-BDC, and (e) PCN-208-NDC at 273 K. (f–j) Selectivities are predicted by IAST for C2/C1 and C3/C1 (0.5:0.5) gas mixtures at 273 K, respectively.

273 and 298 K and 1 bar. It should be pointed out that the PCN-206 series exhibits a better performance compared to those of PCN-207, PCN-207-BDC, and PCN-208-NDC. The adsorption capacities of PCN-206 for  $CH_4$  (12.6 cm<sup>3</sup>

 $g^{-1}$ ),  $C_2H_2$  (104.7 cm<sup>3</sup> g<sup>-1</sup>),  $C_2H_4$  (86.9 cm<sup>3</sup> g<sup>-1</sup>),  $C_2H_6$  (98.7 cm<sup>3</sup> g<sup>-1</sup>), and  $C_3H_6$  (115.2 cm<sup>3</sup> g<sup>-1</sup>) are comparable to those of UTSA-35a and UTSA-36a at 298 K and 1 bar (Figure 8). The reason may come from the suitable pore size

distribution regulated with the *scu* topology and the affinity of the pore surface for adsorbents. Thus, PCN-206 exhibits the best performance for light hydrocarbon storage. More interestingly, the  $CH_4$  adsorption amounts are much less than those of C2 and C3 hydrocarbons under the same conditions.

The PCN-206, -207, and -208 series are saturated with C3 hydrocarbons at lower pressures, and the slopes of adsorption isotherms are much steeper than that of CH<sub>4</sub>, indicating the stronger affinity between higher hydrocarbons and the pore surfaces. Such great differences in adsorption amounts and the interactions between higher hydrocarbons and CH<sub>4</sub> indicate that the PCN-206, -207, and -208 series may realize highly selective separations of CH4 from C3 hydrocarbons. IAST is used to predict the selectivity of binary mixtures of C<sub>2</sub> or C<sub>3</sub> hydrocarbons with CH<sub>4</sub> (molar ratio 50:50) at 298 or 273 K, respectively (Figure 8, Figures S25 and S26). Among them, PCN-207-BDC showed relatively high selectivities of 20.13, 27.46, 32.51, and 244.0 for C<sub>2</sub>H<sub>2</sub>/CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>/CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>/  $CH_4$ ,  $C_3H_4/CH_4$ , and  $C_3H_6/CH_4$  at 298 K (Figure S25). With the decrease in temperature, the selectivities of  $C_2H_2/CH_4$ ,  $C_{2}H_{4}/CH_{4}$ ,  $C_{2}H_{6}/CH_{4}$ ,  $C_{3}H_{4}/CH_{4}$ ,  $C_{3}H_{6}/CH_{4}$  (0.5:0.5) increased significantly to appreciable values of 76.71, 43.17, 92.07, and 1575.36 at 273 K. The selectivity of C<sub>3</sub>H<sub>6</sub>/CH<sub>4</sub> is higher than the corresponding values of MOFs. Moreover, the adsorption enthalpies of PCN-207 and PCN-207-BDC are also higher than those of the other PCN-206 and -208 series (Figure S27). For example, the adsorption enthalpy of  $C_3H_6$  of PCN-207-BDC can reach 60 kJ/mol, which is much higher than the 19 kJ/mol for PCN-206. This may be due to the cage of 207-BDC being more conducive to the selection and screening of gas molecules. The introduction of BDC increases the rigidity of the crystals. At the same time, the insertion of the BDC increases the selection selectivity ratio of  $C_3H_6/CH_4$ from 244 to 1575, and there is a certain increase in the adsorption enthalpy of C3H6 and a decrease in the same parameter for CH<sub>4</sub>.

# CONCLUSIONS

We have successfully fabricated and characterized a series of stable Zr-MOFs with different topology with H<sub>4</sub>TPTA and have calculated and explored the factors that affect different aspects of crystal design synthesis. The flexibility of the ligand leads to the variability of the distance and the distortion of the skeleton, the suitable distance and unsaturated Zr<sub>6</sub> cluster, and the amount of modulating agent. The type and dosage of the second modulating linkers can affect the formation of different configurations. The PCN--206, -207, and -208 series show permanent porosity and excellent thermal and chemical stabilities. Because of the differences in structure, PCN-206 has the highest adsorption capability of light hydrocarbons; moreover, PCN-206 exhibits ultrahigh 2,4-D and DCF adsorption capacities. The PCN-207 series exhibits a superior  $C_3H_6$  adsorption enthalpy and  $C_3H_6/CH_4$  selectivity over those of the other two series, meaning that this type of structural design has a potential C<sub>3</sub>H<sub>6</sub> adsorption capacity.

# ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.9b02950.

Experimental procedures, single-crystal X-ray crystallography analysis,  $N_2$  sorption isotherms, and supplementary figures and tables (PDF)

# Accession Codes

CCDC 1811246, 1965804, and 1879626 contain the supplementary crystallographic data for this article. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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#### Notes

The authors declare no competing financial interest.

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