Flexible Zirconium MOF as the Crystalline Sponge for Coordinative Alignment of Dicarboxylates

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ABSTRACT: Because of their permanent porosity and unparalleled structural diversities, flexible metal–organic frameworks (MOFs) are promising and highly desirable in host–guest chemistry. In this work, we employed a flexible Zr-MOF system, namely PCN-700 species, as the crystalline sponge for guest inclusion. A family of linear dicarboxylate ligands was adsorbed in the void space of PCN-700, which were subsequently confirmed by crystallographic observation. The stretching degree of the PCN-700 series was varied by means of dicarboxylate encapsulation through coordinative alignment.

KEYWORDS: crystalline sponge, metal–organic framework (MOF), flexibility, guest encapsulation, zirconium, coordination bond

INTRODUCTION

With the development of X-ray diffraction technique, the structures of more and more compounds were reliably determined at atomic level.1,2 However, X-ray diffraction method would be limited because it is not applicable to noncrystalline samples in principle. In 2013, Fujita et al. demonstrated a groundbreaking work that introduce a technique to overcome the inherent limitations of single-crystal X-ray diffraction, termed as the crystalline sponge method.3 In their work, the structures of absorbed target guest molecules were clearly determined by crystallographic analysis along with the host frameworks. With this revolutionary approach, not only did researchers realize the structural determination of molecules that hardly crystallize4−6 but they also determined the absolute configuration of natural products and transient species of several reactions.7−10

Metal–organic frameworks (MOFs, also known as porous coordination polymers or PCPs) are an emerging class of porous materials with periodic ordered structures constructed from metal-containing nodes (metal ions or clusters) and organic linkers.11−25 In recent years, MOFs have caught increasing attention and become one of the fastest growing areas in synthetic chemistry and material science, because of their structural and functional tunability.26,27 Apparently, MOFs with easily tuned pore features show great promise for targeted molecular recognition through well-defined pore spaces and environments.28−30 In this regard, MOFs are favorable for the study of guest inclusion behaviors, because of their potential in exhibiting a single-crystalline nature, allowing for the structural characterization of the framework with a high degree of accuracy.31−34 In most cases of crystalline sponge study, guest molecules are presented with the hydrogen bonds or van der Waals interactions of the host frameworks.

Inspired by the above-mentioned outstanding findings, we were intrigued by the possibility of employing the crystalline sponge method for the soaking of dicarboxylate ligands, thus offering a unique opportunity to adsorb linear dicarboxylate fragments by coordination bonds. PCN-70035 adopts a flexible octahedral cage structure, which makes it possible to accommodate guest molecules with shrink nature. In addition, the terminal −OH/H2O moieties coordinated to Zr sites can be substituted by carboxylate groups via an acid-base reaction. Meanwhile, as a Zr-MOF, PCN-700 owns superior stability owing to the strong affinity between Zr(IV) and carboxylate-O atoms from Pearson’s hard/soft acid/base concept.38,39 These three points promote us to develop the flexible PCN-700 to be an ideal platform as crystalline sponge.

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RESULTS AND DISCUSSION

A family of linear organic dicarboxylate compounds with different lengths and functional groups, that is, squaric acid (H₂SA), 2,5-dihydroxyterephthalic acid (H₂DOBDC), muconic acid (H₂MA), 3,3′-dihydroxy-[1,1′-biphenyl]-4,4′-dicarboxylic acid (H₂DOBPDC), and (E)-4,4′-(diazene-1,2-diyl)dibenzoic acid (H₂AZDC), were chosen for the crystalline sponge study. When PCN-700 was immersed in a solution containing different linear carboxylate compounds, PCN-700 exhibited an excellent sponge-like behavior. The carboxylate compounds were adsorbed in the flexible cages of PCN-700. The resulted compounds, namely, PCN-700-SA, PCN-700-DOBDC, PCN-700-MA, PCN-700-DOBPDC, and PCN-700-AZDC, maintain adequate crystallinity following guest encapsulation, which were subsequently analyzed by single-crystal X-ray diffraction. The crystallographic data were summarized in Table S1.

X-ray diffraction analysis indicates that PCN-700-SA, -DOBDC and -DOBPDC crystallized in P4₂/mmc space group, and PCN-700-MA and -AZDC in P4₂/nmc space group, respectively. The similar frameworks of these final products derived from PCN-700, in which each Zr₆ cluster was connected to eight Me₂-BPDC fragments above and below the equatorial plane. In PCN-700-SA, two SA fragments were hanging on a Zr₆ cluster instead of four terminal −OH−/H₂O groups (Figure 2a). In addition, the eight terminal −OH−/H₂O groups can be fully substituted by four SA fragments (noted as PCN-700-SA₄) if there is enough immersion time (Figure S1). This may be assigned to the suitable match size between SA moiety and the pocket of PCN-700. Like the case in PCN-700-SA, DOBDC moieties were hanging to Zr₆ clusters as terminal ligands but with a chelating mode in PCN-700-DOBDC (Figure 2d). In these two products, SA and DOBDC fragments, resided in the pocket of crystalline sponge, play the role of terminal ligands, and such connectivity does not make a change on the topology of the whole framework. In PCN-700-MA, the carboxylate groups of MA were bridged to two adjacent Zr₆ clusters (Figure 2e). MA fragments support the PCN-700

Figure 1. Octahedral cage in PCN-700. All hydrogen atoms were omitted for clarity.

Figure 2. Comparison of PCN-700 structures after the encapsulation of a series of dicarboxylates: (a) PCN-700-SA, (b) PCN-700-FA, (c) PCN-700-BDC, (d) PCN-700-DOBDC, (e) PCN-700-MA, (f) PCN-700-NDC, (g) PCN-700-BPDC, (h) PCN-700-DOBPDC, and (i) PCN-700-AZDC. All hydrogen atoms were omitted for clarity.
structure just like the jack screws support the scissor jack. The similar connection mode has been encountered in our previous work (Figure 2b, c, f, and g). In that case, we have demonstrated that the crystal height along c-direction can be tuned by varying the lengths of ligands, which is similar to a scissor jack that can be lifted and lowered by driving screws. And the channel size along a-axis is directly correlated to the linear linker length. Like the chelating coordination mode of DOBDC, DOBPDC also adopted a chelating mode to connect with Zr6 clusters in PCN-700-DOBPD (Figure 2h). However, both the two ends of DOBPDC were bonded to Zr sites due to the size match between cage and DOBPDC. Interestingly, DOBPDC connected two adjacent Zr6 clusters in a double bridge mode. As a result, a rigid framework was formed, deriving from the flexible parent PCN-700-Me2. From the topological point of view, the overall framework of PCN-700-MA and -DOBPD was transformed from a flexible bcu net to a rigid bct net. In PCN-700-AZDC, AZDC fragments were bonded to Zr sites in the same orientation with Me2-BPDC (Figure 2i). In this sense, the overall framework of PCN-700-AZDC does not change from the topological viewpoint.

These dicarboxylate compounds can be adsorbed in the cage of PCN-700 in an ordered array, but with different modes, perhaps can be assigned to their different lengths in the presence/absence of −OH groups. From the X-ray diffraction analysis, we can see that the 1D channel that perpendicular to the ab plane is almost unchanged before and after the sponge-like behavior of PCN-700 (Figure S2). However, the channel size along the a-axis direction varied with the linker length and functional groups (Figure 2 and Figure S3), and the guest encapsulation induce a more or less unit cell dimension change (Table 1). The length of SA (3.22 Å) is half of the distance between two adjacent Zr6 clusters in pristine PCN-700 (6.98 Å), so two SA fragments were encapsulated in one cage. Owing to interactions of these two SA fragments, the framework was a little opened up to 8.06 Å in PCN-700-SA (Figure 2a). However, the adsorption of FA (fumarate, 4.95 Å) squeezes the framework of PCN-700 owing to its proper length and inherent flexibility (Figure 2b). Although DOBDC possesses a similar length with BDC (1,4-benzenedicarboxylate), the connection modes were different between pristine PCN-700 and guest molecules resulting from the presence of −OH groups (Figure 2c, d). In addition, two DOBD fragments were adsorbed in the cage due to its hanging feature, thus the framework was opened up (17.0 Å), which is larger than that of PCN-700-BDC (14.9 Å). With the encapsulation of MA, the channel size did not change by a large amount like the case of BDC (Figure 2e), whereas the rigid linear NDC (2,6-naphthalene dicarboxylate) and BPDC (4,4′-biphenyldicarboxylate) without substituents obviously open up the frameworks (Figure 2f, g). Compared with DOBDC, DOBPDC adopted a similar chelating fashion residing in the cage but served as bridging linkers to support the framework because of its larger size (Figure 2h). However, the level of opening up the framework by sorption of DOBPDC is evident smaller than that of BPDC, resulting from their different coordination modes. Although the length of AZDC is larger than that of BPDC, the structure of PCN-700-AZDC did not change (Figure 2i), which can be assigned to its same coordination orientation with Me2-BPDC.

To confirm spongelike effect, the reproducible positioning of the guest molecules within the unit cell has been performed. The crystalline sponge, PCN-700, can absorb target molecules from their solution into the pores, because of the molecular-recognition ability of the pores, rendering the incoming molecules to adopt a preferential arrangement in the crystal. After the encapsulation of different dicarboxylate compounds, the structural stability and porosity of resultant samples was retained, as confirmed by the N2 adsorption experiments (Figure S4). These results suggest that dicarboxylate linkers with different lengths in the absence/presence of hydroxyl groups can be adsorbed into the voids formed between adjacent Zr6 clusters. On the one hand, the presence of replaceable sites on the host framework, namely the Zr sites coordinated to −OH /H2O groups, is necessary in the present study. On the other hand, the flexibility of PCN-700 makes it successful to be employed as a crystalline sponge through coordination bond interactions. Furthermore, the 1H NMR measurement was carried out to determine the amounts of guest molecules (Figures S5–S8). From the 1H NMR spectra, we can see that the results of PCN-700-DOBDC and -DOBPDC were in good agreement with the single-crystal X-ray diffraction data (Table S2). However, the contents of MA and AZDC in PCN-700-MA and -AZDC measured by 1H NMR technique were higher than those by X-ray diffraction results. This result perhaps can be assigned to the presence of disordered MA and AZDC in the cages of PCN-700-MA and -AZDC.

## CONCLUSIONS

In conclusion, we performed a systematic study on a flexible Zr-MOF as a crystalline sponge and demonstrated that linear dicarboxylate compounds with different lengths and functional groups can be encapsulated into the void of PCN-700. Single-crystal X-ray diffraction analysis was employed to study the single-crystal-to-single-crystal guest inclusion. The present research expands the potential ability of MOFs as the crystalline sponge to adsorb dicarboxylate compounds through coordination bonds, and the positions of guest molecules can be obtained by X-ray crystallography. More investigation is currently underway in our lab.

## ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.6b16264.

Experimental details, figures, and tables (PDF)

Crystallographic data (CIF)

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