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Short communication

The roles of rod-packed organic units for preparing stable porous coordination polymers with carboxylate ligands

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ABSTRACT

Despite tremendous efforts, designing and preparing water, chemical, and moisture stable porous coordination polymers (PCPs) with carboxylate ligands remain a challenge. Here, we firstly and systemically investigated the roles of rod-packed organic units for preparing the stable PCPs with different carboxylate ligands. The experimental results demonstrated that the rod packed organic units with short distance of adjacent ligands, bridged by La^{3+} metal chain, can form water, chemical, and moisture stable PCPs.

In recent years, the fascinating discovery in the area of functional, nanostructured materials is the emergence of large numbers of structurally defined porous coordination polymers (PCPs) [1,2]. Their versatile architectures and customizable chemical properties could enable them to be attractive candidates for gas storage [3–7], separation [8–10] and catalysis [11,12].

Water, chemical, and moisture stabilities are important factors for any sorbent that has potential to be used for practical applications, especially for PCP materials [13–19]. Till now, almost twenty thousand of PCPs have been reported [20]; however, unfortunately, some of the most promising PCPs are limited because of instability with respect to moisture and water [4,21,22]. Therefore, for offering an opportunity to address this problem, it is essential to find and understand the factors that affect the stability of porous frameworks, especially for the framework with carboxylate ligands.

PCPs are crystalline materials consisted of metal ions/clusters and organic ligands, which are bridged together to form extended porous frameworks. The stability of PCPs should be dominated by the strength of coordination bonds between ligands and metal centers. Generally, the methods for enhancing the strength or preventing the corrodibility of coordination bonds were believed as rational ideas for accessing stable frameworks [23]. For example, by introducing hydrophobic alkyl-chains around coordinate sites, IRMOF-1 showed an enhanced moisture-resistant [24]. Additionally, the rational-design methods of postsynthetic modification and polymer coating can produce moisture/water-resistant and superhydrophobic PCPs with intact porosity [25,26]. Further, the strategy of using polyazolate-bridging ligands can lead to frameworks with strong metal–nitrogen bonds, providing a greater chemical and thermal stability compared to their carboxylate-based counterparts [13]. However, the generated water and moisture stable PCPs by employing the above methods will suffer the decreasing of their pore size and volume, and further, some approached only feasible to some specific PCPs.

Very recently, we reported two La-based PCPs with easily-prepared carboxylate ligands [16,17]. Their good water and chemical resistance encouraged us to speculate that the coordination of ahighly-coordinated metal center (from conventional 4 or 6 to 8 or 9) with rod-packed organic units may be a new method to prepare stable PCP, because the increase of connectivity can possibly improve the strength of connection between metal clusters and ligands, and more importantly, the well-packed organic units could provide a tight space for preventing the attack of M–O bonds from water or moisture. If this idea works well, it will definitely facilitate the design and preparation of stable PCPs with such great number of carboxylate ligands.

We are interested in the construction of porous coordination polymers with interesting properties based upon carboxylate ligands [27–29]. Herein, in order to confirm this idea, four La-based PCPs (La–BTC, La–BTB-1, La–BTB-2, La–BTN) with three different carboxylate ligands (1,3,5-Benzenetricarboxylic acid: H_3BTC; 1,3,5-Tris(4-carboxyphenyl)benzene:H_3BTB; 1,3,5-Tri(6-hydroxycarbonylnaphthalen-2-yl) benzene: H_3BTN) were synthesized and structurally characterized. Powder X-ray diffraction pattern (PXRD) and gas adsorption experiments of treated samples

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demonstrated that the noticeable variation of structural stability should be attributed to different types of ligand arrangements along metal chains.

These four PCPs were solvothermally synthesized from a mixture of $La(NO_3)_3 \cdot 6H_2O$ and H_3BTC, H_3BTB and H_3BTN in different solvent systems, respectively (Fig. 1). Two of them (La–BTN and La–BTB-1) as reported in our previous work [16,17] and the third one (LaBTB-2) were prepared according to Walton's work [30]. The phase purities of the PCPs were confirmed by PXRD. The new structure of La–BTC was determined by single-crystal X-ray diffraction analysis. Thermogravimetric analyses (TGA) show that the four PCPs are thermally stable up to 400 °C under N_2 atmosphere.

Single crystal X-ray diffraction revealed that the structure of $[La(BTC)(H_2O)]_3 \cdot x$Guest is chiral, with the space group of $P4_3$. The asymmetric unit of it consists of one La^{3+} ion, one BTC ligand and one coordinated water. The La^{3+} ion is nine-coordinated and binds to eight oxygen atoms from six different BTC^{3-}ligands and one water molecule. Each BTC^{3-}ligand connects to six different La^{3+} ions. The $LaO_8(H_2O)$ polyhedra are connected by corner-sharing to form a chiral of –La–O–C–O–La– along the *c*-axis. These chains are bridged together by the BTC^{3-}ligands to form a 3D framework (Fig. 1a), with the pore size of 7×7 Å^2.

By comparing these four structures, we found that the space groups of them are all chiral. All of the coordination geometries of the La center were completed by eight oxygen atoms from six different carboxylate groups and one coordinated water/DMF molecule. The metal–oxygen chains with closed La/La distances of 4.224 to 4.293 Å were bridged by BTC, BTB and BTN ligands in those series of PCPs (Fig. S8). However, it is worth noting that the arrangements of the ligands in them show significant differences. For La–BTC, the adjacent BTC moieties adopt the end-to-end type, while that in other compounds took the face-to-face type. For La–BTB-1, the distances between the adjacent benzene rings are around 4 Å, which means that there is no enough space for any extra guest molecules (even including H_2 molecules) to go inside between every two adjacent benzene rings. Thus, the well-packed benzene rings with a high concentration of protons act like a wall that can provide a hydrophobic environment along the channel. However, the extended distance of adjacent ligands was found in La–BTN and La–BTB-2 (Fig. 2). Therefore, we can theorize that the coordination geometries of La^{3+} completed by rod-packed units with different distances will bring the PCPs with varied water and moisture resistance.

Although three of the structures have been reported, their water, chemical, and moisture stabilities, especially at high temperature, have not been well explored. Further, the roles of rod-packed organic units in influencingthe stabilities of PCPs have also not been reported before. Thus, systemic study of the stabilities of those four La–PCPs is very necessary. Generally, the combined results show that PXRD and gas adsorption were the most effective methods for indentifying the integrity of porous materials. The frameworks with high stability should keep their original PXRD patterns, as well as their gas uptake capacities.

The fresh samples of those four PCPs were soaked in hot (60 °C and 100 °C) aqueous HCl ($pH = 2$), aqueous NaOH ($pH = 12$) and pure water for 24 h. After the temperature cools down, part of the samples was used for PXRD pattern collection (Figs. S9–S12) and the rest of them were used for gas sorption experiments (exchanged by methanol for three times and degassed at 120 °C for 24 h, Figs. S14–S17). As shown in Figs. S9–S12, the framework of La–BTC transformed to another unknown phase, whereas, the PXRD patterns of La–BTB-1, La–BTB-2, and La–BTN matched well with their original form, indicating the integrity of their frameworks. Meanwhile, the gas adsorption results demonstrated that treated La–BTC did not show any gas uptakes at low pressure range. The very low amount of gas uptake in it at around 95 kPa should be ascribed to the adsorption of apertures between particles. Thus, La–BTC cannot maintain its porosity under such condition. For La–BTB-2, the gas uptake of treated samples decreased from $300\ cm^3 \cdot g^{-1}$ to ~$20\ cm^3 \cdot g^{-1}$ as well as the disappearance of gate opening at $P/P_0 = 0.3$, even if the PXRD pattern of the samples remained the same after treatment. Interestingly, for La–BTN, the gas uptake of treated samples ($pH = 2$ and 12) at 100 °C just decreased a little, and moreover, the gas uptake of La–BTN ($pH = 7$) is nearly the same as that of the fresh one, exhibiting a good integrity of the framework. Moreover, the treated La–BTB-1 maintained the same gas uptakes as its fresh sample, except for the sample that was treated under acid solution ($pH = 2$) at 100 °C.

To further explore the stability of these materials, we treated the activated sample of them at 80 °C and 80% RH for 24 h. The PXRD patterns (Figs. S9–S12) and gas uptakes (Figs. S18–S21) of the samples reveal that La–BTC transforms to that unknown phase without porosity

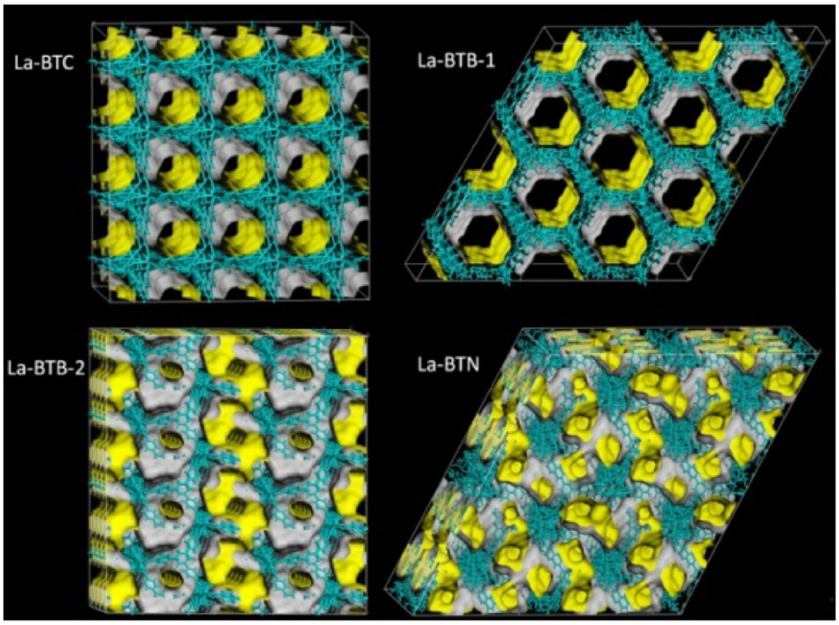

Fig. 1. The packing view of those four PCPs (inner surfaces: yellow, outer surfaces: gray).