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Protection and Deprotection Approach for the Introduction of Functional Groups into Metal−Organic Frameworks

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Great progress has been made during the past two decades in the construction of metal−organic frameworks (MOFs) comprising an infinite alternate arrangement of metal ions and bridging ligands.[1] Because of the high regularity of their pores, MOFs are potentially useful for their gas storage[2] and catalytic[3] properties. Modification of the frameworks has recently attracted much interest because interactions between guest molecules and host frameworks critically affect these properties. Unsaturated metal centers (UMCs)[4] or functional groups on the organic bridging ligands[5] have been introduced into the frameworks. Several approaches for introducing UMCs to the frameworks have been reported. Functionalization of the organic ligand is limited, however, because some kinds of functional groups have a tendency to coordinate to metal ions. For example, the hydroxyl and carboxyl groups in 2,5-dihydroxyterephthalic acid (H_2dhybdc) have a tendency to coordinate to metal ions in a bidentate fashion, affording a chelated compound.[6]

Use of a postsynthetic method may be useful for functionalizing MOFs. The research groups of Cohen, Cronin, Gamez, and Yaghi have reported the modification of amino or aldehyde groups in MOFs, and various functional groups were introduced using "click chemistry" by Sada and co-workers.[7]

However, there are difficulties associated with postsynthetic methods. Pore volume is decreased by a functionalization reaction, and the gas absorption capability can be reduced. A functionalization reaction commences at the peripheral part of the crystals, and transport of a reactant to the central part tends to be hindered by a decrease in the pore diameter.

Here we propose a three-step procedure for introducing noncoordinating hydroxyl groups of dhybdc into MOFs. The three steps include the following: (a) a presynthetic reaction, i.e., protection of the functional groups by introduction of protecting groups; (b) a complexation reaction of a MOF, and (c) a deprotection reaction as a postsynthetic process. Figure 1 is a schematic representation of this protection−complexation−deprotection (PCD) process. Here we report the first application of the PCD method, in the synthesis of [Zn(dhybdc)(bpy)]·4DMF (**1**) (bpy = 4,4′-bipyridine, DMF = *N*,*N*-dimethylformamide). Single-crystal X-ray diffraction measurements revealed that the noncoordinating hydroxyl group was successfully introduced into the MOF.

First, we protected each hydroxyl group with an acetyl group. Given its moderate stability, it is suitable for protection and deprotection reactions. 2,5-Diacetoxyterephthalic acid (H_2dacobdc) was prepared by the acetylation of hydroxyl groups with acetic anhydride [see the Supporting Information (SI)]. In the second step,

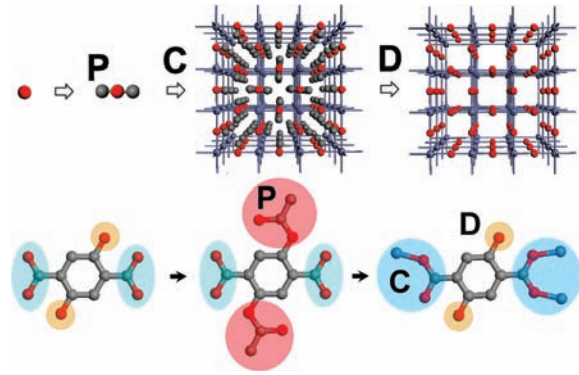

Figure 1. Schematic illustration of the steps in the protection−complexation−deprotection (PCD) method for preparing MOFs.

the reaction of H_2dacobdc, $Zn(NO_3)\cdot 6H_2O$, and bpy in DMF afforded good block crystals of **1**.

The structure of **1** was determined by single-crystal X-ray diffraction analysis, the details of which are given in the SI. **1** has a pillared-layer structure (Figure 2) in which each two-dimensional (2D) layer consists of a square grid of dimeric Zn bridged by the dhybdc. One carboxylate of each dhybdc coordinates in a monodentate fashion to one zinc ion, and the other carboxylate coordinates to two separate zinc ions (Figure 3a). Thus, each zinc ion has a trigonal bipyramidal coordination geometry, with one monodentate carboxylate oxygen atom, two bridging carboxylate oxygen atoms, and two nitrogen atoms from the bpy pillars (Figure 3b). The coordination geometry in **1** is different from those in the usual coordination compounds of zinc ions with dhybdc[5] and in pillared-layer MOFs previously reported for the terephthalate derivatives.[8]

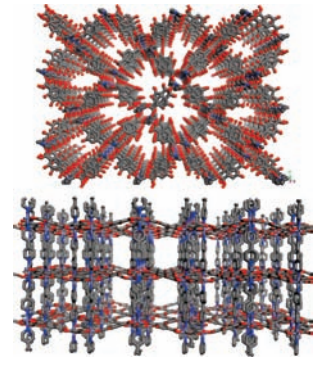

Figure 2. Crystal structure of **1**: (top) view along the *c* axis; (bottom) perspective view of 2D layers and bpy pillars. Solvent molecules have been omitted for clarity.

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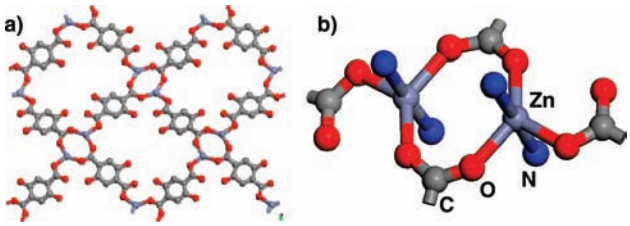

Figure 3. (a) Crystal structure of **1** in the *ab* plane. (b) Coordination geometry of zinc ions. Solvent molecules have been omitted for clarity.

Unexpectedly and fortuitously, the acetoxyl groups were totally removed, and the dhybdc ligand was observed in **1**, indicating that the C and D reactions were one-pot reactions and that the noncoordinating hydroxyl groups were successfully introduced into the cavities. Each hydroxyl group of the ligand is intramolecularly hydrogen-bonded to an adjacent carboxylate group and contributes to the stabilization of the 2D layer structure of **1**. Intermolecular hydrogen bonds are also formed between two dhybdc ligands, which seem to cause a distortion of the 2D sheet of Zn(dhybdc). The stretching mode of the hydroxyl group was observed at 3450 cm^{-1} in an infrared spectrum of **1**, confirming the presence of noncoordinated hydroxyl groups (see the SI). Four DMF molecules are captured in each crystal lattice.

The deprotection conditions of the H_2dacobdc ligand were examined by NMR analysis (see the SI). It was found that the deprotection rate is very low under the conditions of MOF preparation, and at least one of the hydroxyl groups is protected before the complexation reaction occurs. The deprotection reaction of the ligands should proceed simultaneously with crystal growth or might occur after the crystal growth. In addition, X-ray powder diffraction peaks corresponding to **1** were not observed in a sample obtained from a mixture of H_2dhybdc, bpy, and $Zn(NO_3)\cdot 6H_2O$.

MOFs consisting of Zn, terephthalate, and bpy form interpenetrated structures, and consequently, only a small pore ($\sim 1 \times 1$ Å) can be introduced.[8b] However, **1** does not display an interpenetrated structure. The tendency to interpenetrate in MOFs is high when the connectors are long, as is the case here, and it is difficult to avoid interpenetration. We are of the opinion that if the acetyl group is present during the complexation, then its bulkiness suppresses the interpenetration. This offers further support for the conclusion that the D process occurs during or after the coordination reaction. Consequently, the PCD method can be used to prevent interpenetration and to obtain materials with larger pores and also wider apertures.

This procedure for the modification of MOFs offers several advantages. Acidic functional groups can be protected from coordination reactions. The modification of acidic groups in MOFs is of significance for tuning the ionic conductivity[9] or cation exchange capability.[10] Bulky protective groups also prevent the interpenetration reaction. Avoidance of the interpenetration reaction is vital for the establishment of pores with controlled aperture diameters, which critically affect the gas selection or molecular motion in the frameworks. After the D reaction, the pore size increases. Enlarged pores may improve transport of reactants and byproducts. The reaction in the MOFs is then expected to run to completion.

To summarize, we have demonstrated a novel reaction strategy for constructing porous MOFs. [Zn(dhybdc)(bpy)]·4DMF was synthesized by a protection−complexation−deprotection (PCD) method. This procedure prevents interpenetration and coordination of hydroxyl groups to zinc ions, and uncoordinated hydroxyl groups were successfully introduced in the pores. Our results showed that the PCD method provides a new strategy for constructing a large pore aperture and introducing a functional group into the framework. Furthermore, this is the first report of the successful introduction of a functional group by a pore-expanding process.

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Supporting Information Available: Synthetic procedures, details of single-crystal X-ray analysis, spectroscopic data, and thermal analysis of **1**. This material is available free of charge via the Internet at http://pubs.acs.org. Structure parameters for compound **1** are available free of charge via Cambridge Crystallographic Data Centre under deposition number CCDC-727233.

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