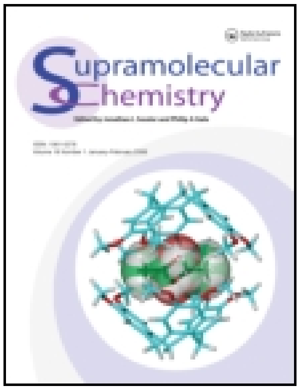

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Synthesis of a novel isoreticular metal-organic framework by protection and complexation of 2,5-dihydroxyterephthalic acid

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Synthesis of a novel isoreticular metal–organic framework by protection and complexation of 2,5-dihydroxyterephthalic acid

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A novel isoreticular metal–organic framework (IRMOF) was synthesised by controlling the coordination ability of the functional groups of a ligand. Hydroxyl groups of 2,5-dihydroxyterephthalic acid (H_2dhybdc) were protected with acetyl groups and complexation reactions of these unprotected H_2dhybdc and protected 2,5-diacetoxyterephthalic acid (H_2dacobdc) were performed with zinc ions. From the X-ray powder diffraction measurement, reaction with non-protected dhybdc results in an amorphous compound, while the compound obtained with protected dacobdc was isostructural to IRMOF-**1**. Hydroxyl groups of the non-protected ligand have the ability to coordinate to the metal sites and random coordination of various types of functional groups resulted in the amorphous compound, while protection of certain groups can prompt the highly ordered MOF.

Keywords: metal–organic frameworks; coordination polymers; protection and deprotection method

Introduction

Metal–organic frameworks (MOFs) have attracted great interest in the past two decades as novel porous materials, because they show large variation in metal species, organic ligands, coordination geometry, aperture diameter and even the shape of the cavity (*1–4*). Their physical and chemical properties have also been widely studied such as gas sorption or separation (*5–7*), optical (*8*), magnetic (*9–11*) and catalytic properties (*12–14*). Recently, many reports have focused on introducing functional groups into MOFs, for the sake of achieving fascinating properties, especially proton conductivity (*15–19*). However, acidic functional groups have a tendency to coordinate to metal sites as well as conventional carboxylate or pyridyl groups, which are often used to construct frameworks of MOFs, and it is still difficult to render some chosen functional groups coordinating while the others are not.

We have reported a novel MOF having non-coordinating hydroxyl groups synthesised by a novel procedure called the protection–complexation–deprotection (PCD) method (*20*). In that paper, we synthesised 2,5-diacetoxyterephthalic acid (H_2dacobdc) by protecting the hydroxyl groups of 2,5-dihydroxyterephthalic acid (H_2dhybdc) with acetyl groups and succeeded in introducing hydroxyl groups into the pillared-layer type MOF using the PCD method. Moreover, the complexation and deprotection reaction occurred in a one-pot reaction, and the resulting product was totally deprotected.

Here, we report a significant intermediate step of the PCD method. Yaghi et al. (*2*) presented highly symmetric MOFs called ‘isoreticular MOFs (IRMOFs)’ with terephthalic acid and its derivatives. We have tried to synthesise IRMOF with H_2dhybdc; however, only an amorphous compound can be obtained. On the other hand, a compound consisting of protected H_2dacobdc was successfully synthesised and characterised to be isostructural to IRMOF by X-ray powder diffraction (XRD) analysis, elemental analyses (EA) and infrared (IR) spectroscopy. From these results, the complexation reaction of H_2dacobdc with zinc ion leads to the novel IRMOF, $[Zn_4O(dacobdc)_3]$ (**1**), while only an amorphous powder can be obtained by the reaction of H_2dhybdc ligand and zinc ion under the same conditions (Figure 1).

Experimental

All chemicals were purchased and used without further purification. H_2dacobdc was synthesised as reported previously (*20*). Thermal gravimetry and IR spectroscopy were performed with TG-DTA 2000SA (Bruker) and NEXUS 670 FT-IR (Thermo Fisher), respectively.

Synthesis of $[Zn_4O(dacobdc)_3]$ $(DMF)_n$ $(1\cdot(DMF)_n)$

Triethylamine (0.5 ml, 3.6 mmol) was added to a stirred solution of $Zn(NO_3)_2(H_2O)_6$ (119 mg, 0.400 mmol) and H_2dacobdc (85 mg, 0.301 mmol) in

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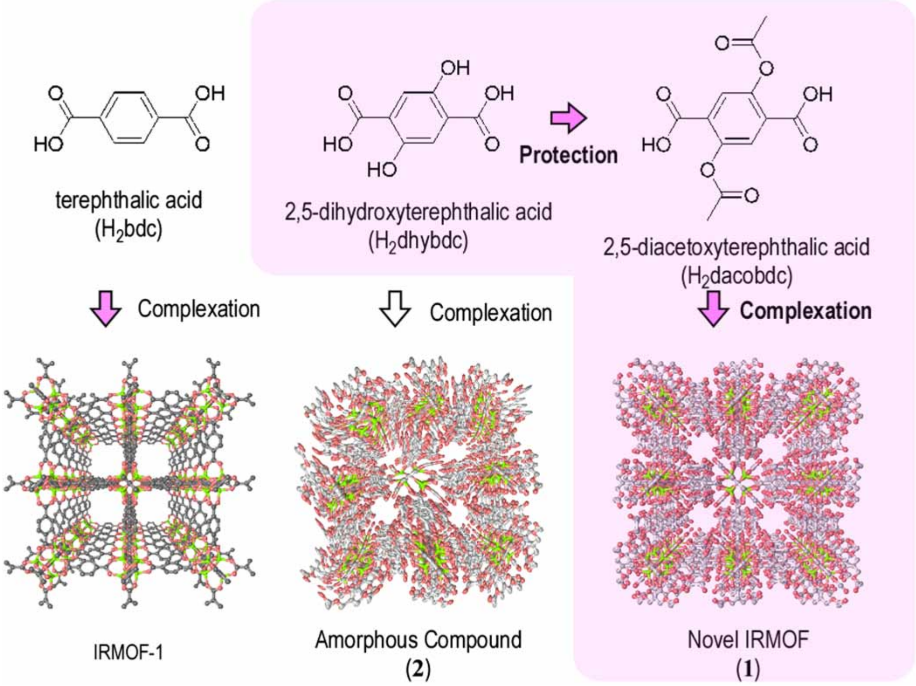

Figure 1. Schematic illustration of protection and complexation method for preparing the MOF.

N,*N*-dimethylformamide (DMF, 10 ml). After 30 s, the white precipitate was filtered off, washed several times with DMF and dried *in vacuo*. A white powder was obtained. EA calcd (found) for $Zn_4O(dacobdc)_3(DMF)_2(H_2O)_4$ (%) were C 37.75 (37.54), H 3.47 (3.58) and N 2.10 (2.18), respectively.

Reactions of terephthalic acid and H_2dhybdc were performed under the same reaction conditions. The resulting white and yellowish powders (IRMOF-**1** and **2**, respectively) were obtained as outlined in Figure 1.

These compounds decomposed when the dried samples were exposed to air; thus, XRD patterns were collected when the compounds were wetted with DMF (Figure 2). EA were performed on evacuated samples before exposure to air.

X-ray powder pattern fitting

XRD measurement of the sample was performed with D8 Advance (Bruker) in Bragg–Brentano geometry using Cu Kα radiation. X-ray powder pattern fittings were carried out using Materials Studio 4.4 (Accelrys, San Diego, CA, USA). Indexing of the space group was carried out with X-Cell, and a reasonable space group was chosen from those suggested. Pearson-VII profile functions, along with Berar–Baldinozzi asymmetry correction parameters, were selected to generate a line shape for the simulated diffraction peaks. The lattice and profile parameters were first refined using the Pawley method before being refined by the Rietveld method (*21*). Peak intensities and background parameters were refined by the Rietveld method. A global isotropic temperature factor was used for the Rietveld refinement (Table 1). For the Rietveld refinement, two DMF molecules were used. The coordination geometry of the MOF was first modelled after IRMOF-**1**, and acetoxyl groups of dacobdc were added for four sites of the terephthalate ligand whose occupancies were fixed at 0.5; therefore, two adjacent acetoxyl groups were visually overlapped. The results of the Rietveld fitting and the fitted structure are shown in Figures 3 and 4, respectively.

Results and discussion

XRD patterns of synthesised compounds and the simulated pattern of IRMOF-**1** from the literature are shown in Figure 2. Only a broad peak at $2\theta = 8^\circ$ was observed for **2**,

Table 1. Results of the Rietveld refinement.

X-ray source	Cu Kα
Composition	$Zn_4O(dacobdc)_3(DMF)_2$
Temperature	*RT*
Wavelength (nm)	λ_1 0.1540562; λ_2 0.1544390
Fitted profile range	5–80°
2θ step increment	0.02886
Space group	*Fm*-3*m*
Lattice parameter a (nm)	2.5880(9)
wR_p (%)	5.66
R_p (%)	4.26

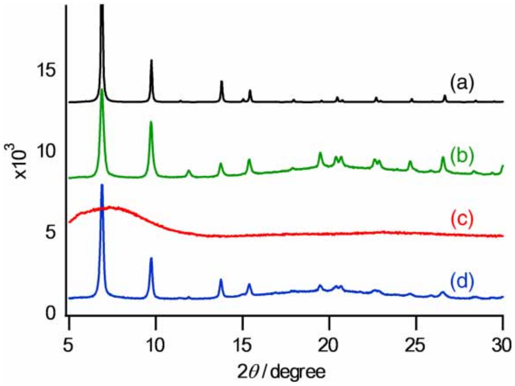

Figure 2. XRD patterns of (a) simulated pattern from the crystal structure of IRMOF-**1**, (b) **1**, (c) IRMOF-**1** and (d) **2**.

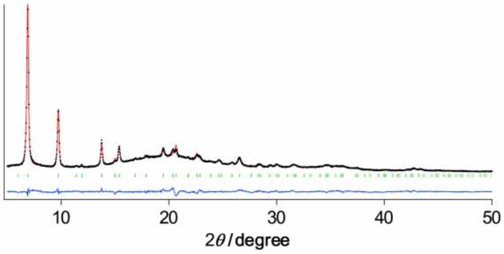

Figure 3. Result of the Rietveld refinement of **1**. Grey line and black dots correspond to simulated and experimental patterns, respectively. Bars at intermediate and bottom black lines correspond to suggested peak positions from the unit cell and the difference between the simulated and experimental data, respectively.

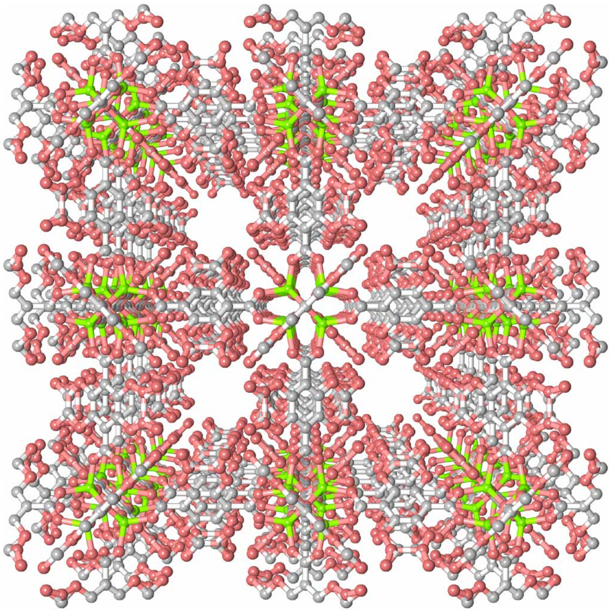

Figure 4. Crystal structure of **1**. Light green, red and grey balls correspond to zinc, oxygen and carbon atoms, respectively. DMF molecules used for the refinement were omitted for clarity.

showing the low crystallinity of the compound. The dhybdc ligand consists of hydroxyl and carboxylate groups, and it is well known that CPO-27-Zn is synthesised by the reaction of H_2dhybdc and zinc ion under solvothermal conditions (*22*, *23*), in which all hydroxyl groups coordinate to zinc atoms. Compound **2** was synthesised at a lower temperature with more rapid conditions than those for CPO-27-Zn, and some of the hydroxyl groups also coordinated to zinc ions as well as carboxylates in a disordered fashion, prompting the uncrystallised compound. In contrast, the XRD pattern of **1** is very similar to that of IRMOF-**1**, indicating that **1** consists of a protected ligand that coordinates to zinc atoms in a highly ordered fashion, even with the rapid synthetic conditions, giving rise to a similar crystal lattice to that of IRMOF-**1**.

The space group of **1** was proposed as *Fm*-3*m* and the lattice parameter was fitted to $a = 2.5880\,\mathrm{nm}$ by the Rietveld method, both of which are in good agreement with IRMOF. The crystal structure of **1** is suggested as shown in Figure 4. As shown in the figure, a highly symmetric MOF was observed and acetoxyl groups did not coordinate to the zinc ions.

The existence of acetoxyl groups in **1** was also confirmed by IR and EA methods. The vibrational mode of the carbonyl group in the acetyl group was observed at $1770\,\mathrm{cm}^{-1}$ in the IR spectrum and the result of EA is in good agreement with the formula; therefore, dacobdc was not deprotected by the coordination reaction. Thus, the IRMOF structure can be constructed by protecting these hydroxyl groups of dhybdc to prevent coordination of hydroxyl groups.

Deprotection reaction was executed; however, this IRMOF was decomposed by water vapour existing in the air as well as the other IRMOFs, which is known to be unstable against nucleophile (*24*). Thus, high stability of a framework is significant to complete the deprotection reaction.

Conclusion

In conclusion, we succeeded in synthesising a novel IRMOF, [$Zn_4O(dacobdc)_3$] (**1**). Compound **1** consists of a protected ligand, dacobdc. Without the protecting hydroxyl groups of dhybdc, only an amorphous compound was obtained. Therefore, acetyl groups act as an impediment for the coordination of hydroxyl groups. This reaction is an important second step of the PCD method, and this result is the first example of identification of the protected compound.

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