

Evaluation of Structural Relationship in Hybridized Porous Coordination Polymer Crystals

Porous coordination polymers (PCPs) or metal-organic frameworks (MOFs) have attracted considerable attention owing to their wide variety of scientific and industrial applications, such as adsorption, separation, and catalysis [1]. Over the past decade, the chemical functionalization of the PCP framework scaffold has been intensively studied to improve their properties. The promising strategy for developing the PCP properties is to integrate several framework structures, thus several functions, into one crystal – the so-called hybridized PCP crystal. The key synthetic protocol is the epitaxial growth of the second crystal that surrounds the core crystal because a lattice match promises pore connections at the interface between two crystals. This class of hybridized PCP crystals allows for systematically tuning the framework composition of both metal ions and organic ligands. The careful choice of components enables us to design the spatial configuration of crystals and their structural relationship, leading to the novel porous property that a single PCP framework never achieves. Here, we demonstrate the syntheses of hybridized PCP crystals by epitaxial growth and the structural relationship between the shell crystal and the core crystal determined using X-ray diffraction analyses at beamline **BL13XU**.

A series of tetragonal frameworks (Fig. 1(a)), $[M_2(\text{dicarboxylate})_2(\text{N-ligand})]_n$, wherein dicarboxylate *layer* ligands link to dimetal clusters to form two-dimensional square lattices, which are connected by dinitrogen *pillar* ligands at lattice points, are good candidates for the hybridization of two distinct PCPs. We have established the systematic hybridization synthesis by a solvothermal method and present here two types of hybridized PCP crystals: heterometallic core/shell crystals (Fig. 1(b)) [2] and hetero-pillar-

ligand sandwich-type crystals (Fig. 1(c)) [3].

The heterometallic core/shell crystal that consists of two different metal ions has been chosen for hybridization: $[Zn_2(\text{ndc})_2(\text{dabco})]_n$ (**1**) as the core crystal and $[Cu_2(\text{ndc})_2(\text{dabco})]_n$ (**2**) as the shell crystal ($a = 10.921(1)$ and $c = 9.611(1)$ for **1**, and $a = 10.8190(3)$ and $c = 9.6348(6)$ for **2**), (ndc = 1,4-naphthalene dicarboxylate, dabco = 1,4-diazabicyclo[2.2.2]octane). Synchrotron X-ray diffraction measurements were performed to investigate the structural relationship between the core crystal and the shell crystal at BL13XU. The core/shell crystal of **1/2** was fixed on a substrate with the *a*-axis oriented upward and diffractions were recorded at a desired Bragg position. The θ - 2θ scan of **1/2** at the initial position ($\chi = 90^\circ$) provided two sharp peaks assigned to *h*00 Bragg peaks and the ϕ scan at the 110 Bragg position gave two sharp peaks every 180° , which were assigned to the 110 and $1\bar{1}0$ Bragg peaks (Fig. 2(a)). These results indicate that the shell crystal was grown on the core crystal as a single crystal.

In the same manner, the core/shell crystal (**1/2**) was mounted with the *c*-axis oriented upward. While the θ - 2θ scan gave only 00*l* Bragg peaks, the characteristic triplet peaks were periodically observed every 90° in the ϕ scan at the 101 Bragg position (Fig. 2(b)). The central peak of each triplet peak was assigned to the 101 or 011 Bragg peak from the core crystal (**1**), whereas the two side peaks ($\Delta\phi_{\text{av}} = |\phi_{\text{cen}} - \phi_{\text{side}}| = 11.7$) were assigned to the diffraction from the shell crystal (**2**). The emergence of the two side peaks implies that two in-plane domains of the shell crystal (**2**) were grown on the {001} surface of the core crystal (**1**) (Fig. 2(c)). The significant difference in lattice constant (*ca.* 0.1 Å) between **1** and **2** is compensated by in-plane

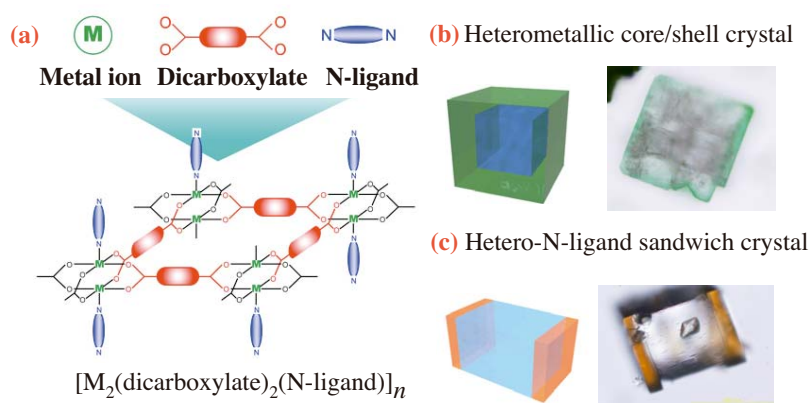


Fig. 1. (a) Schematic illustration of series of frameworks, $[M_2(\text{dicarboxylate})_2(\text{N-ligand})]_n$. Optical microscopy images and schematic illustrations of hybridized crystals of (b) **1/2** and (c) **1/3**.

rotational epitaxial growth. Such a rotational structural relationship at the crystal interface can eventually work as a filter for the separation of guest molecules.

On the other hand, the choice of two different pillar ligands for hybridization leads to the fabrication of sandwich-type crystals; $[\text{Zn}_2(\text{ndc})_2(\text{dabco})]_n$ (**1**) as the core crystal and $[\text{Zn}_2(\text{ndc})_2(\text{dpndi})]_n$ (**3**) as the second crystal ($a = 10.921(1)$ and $c = 9.611(1)$ for **1**, and $a = 10.906(2)$ and $c = 22.456(4)$ for **3**, $\text{dpndi} = N,N'$ -di(4-pyridyl)-naphthalenetetracarboxydiimide). This is because the secondary crystal growth at the $\{100\}$ surface of the core crystal consisting of ndc and dabco was inhibited by mismatch of molecular lengths between dabco and dpndi . The second crystal **3** could only be grown at the $\{001\}$ surface that consists of only the common component ndc .

The synchrotron X-ray diffraction measurement of the sandwich-type crystal (**1/3**) fixed on a substrate with the c -axis oriented upward was performed to successfully obtain two shape 00ℓ peaks from both **1**

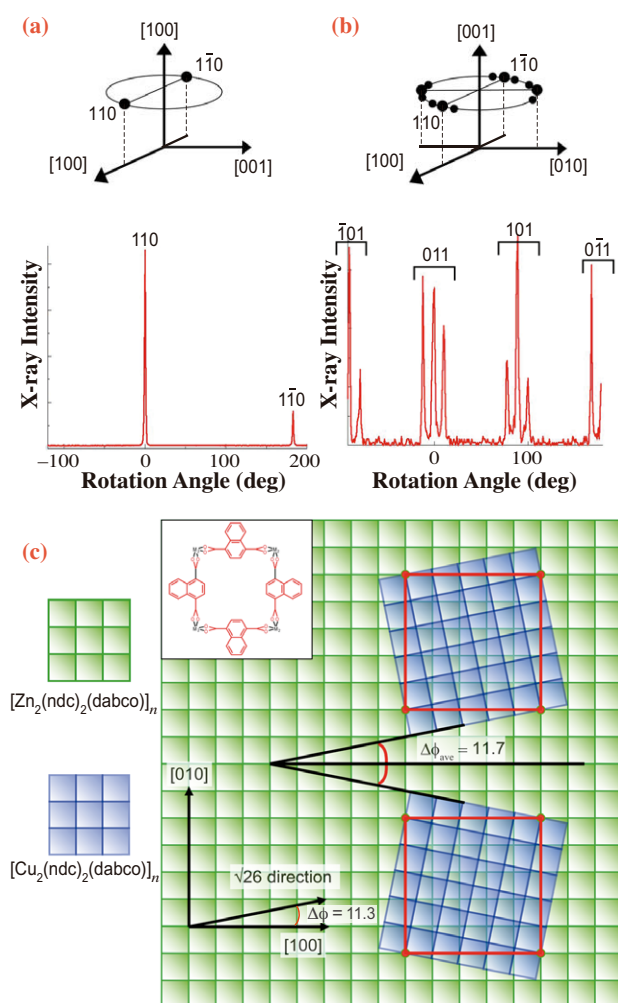


Fig. 2. Scan of rotation angles around (a) $[100]$ ϕ scan and (b) $[001]$ directions. (c) Schematic model of structural relationship between core lattice and shell lattice on (001) surface.

and **3** crystals in the θ - 2θ scan. The ϕ scan at the 101 Bragg position gave four sharp peaks, which were assigned to the 101 , 011 , $\bar{1}01$ and $0\bar{1}1$ Bragg peaks (Fig. 3). The correspondence of the ϕ angles between **1** and **3** indicates that the second crystal (**3**) was grown epitaxially on the core crystal (**1**) with a perfect lattice match at the $\{001\}$ surface. Unlike the heterometallic system (**1/2**), the negligible difference in lattice constant (ca. 0.015 \AA) ensures pore connection at the crystal interface.

On the basis of the presented results that opened the way to unveil the structural relationship of hybridized PCPs, the crystals with various properties, such as adsorption and separation, are considered suitable for integration into a single crystal, resulting in the fabrication of “multifunctional PCPs.”

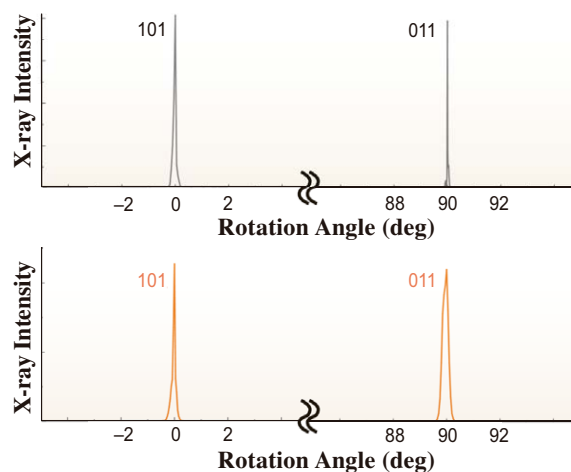


Fig. 3. Scan of rotational angles around $[001]$ directions (ϕ scan) of (a) core crystal **1** and (b) second crystal **3**.

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