

Crystal conversion between metal-organic frameworks with different crystal topologies for efficient crystal design on two-dimensional substrates

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ABSTRACT

Crystal conversion of metal-organic frameworks (MOFs) between different crystal topologies on a polymer substrate has been successfully achieved by localized dissolution of MOF crystals followed by a rapid self-assembly of framework components. Upon addition of the desired organic linkers to the reaction system containing MOF crystals on the substrate, reversible crystal conversion between the $[\text{Cu}_2(\text{btc})_3]_n$ and $[\text{Cu}_2(\text{ndc})_2(\text{dabco})]_n$ frameworks (btc = 1,3,5-benzene tricarboxylate, ndc = 1,4-naphthalene dicarboxylate, dabco = 1,4-diazabicyclo[2.2.2]octane) could be routinely achieved in high yields. Most surprisingly, in the case of conversion from the $[\text{Cu}_2(\text{ndc})_2(\text{dabco})]_n$ to $[\text{Cu}_2(\text{btc})_3]_n$ frameworks, the $[\text{Cu}_2(\text{btc})_3]_n$ crystals with unique shapes (cuboctahedron and truncated cube) could be prepared using butanol as a reaction medium.

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1. Introduction

Over the past decade, metal-organic frameworks (MOFs) have captured the attention of many researchers because of their potential for use in gas storage [1,2], separation [3,4], sensing, and catalysis [5,6]. The MOF properties that depend on the crystal structure, pore size, pore shape, and composition have been well explored, especially for materials prepared by solvothermal methods. The properties of MOFs are strongly dependent on the crystal structures and crystal topologies, and are sensitive to the chemical functionalities of metal ions and organic ligands [7–9]. The strong dependence of the properties of MOFs on the nanopore size and chemical functionalities has been utilized in MOFs based on selective molecular sensing and separation. In recent years, a post-synthetic approach for preparing MOF crystals has attracted considerable attention because the design of the nanopore size and chemical functionalities of the frameworks can be readily controlled by replacing the metal ions or organic ligands [10–13].

Solid-solid crystal conversions in MOFs are of great importance for providing nanostructures themselves and as novel pathways to produce new MOF crystals [14–21]. To date, there have been

diverse reports on solid-solid conversion in MOF crystals by adding other metal ions or organic ligands to a reaction solution containing parent MOF crystals. Successful conversion of MOF crystals by solvent-assisted linker exchange has been reported [14,15,22–24]. A complete structure and composition evolution of the frameworks can be achieved by replacing the initial metal ion/organic ligand and desired metal ion/organic ligand. Similarly, crystal reconstruction of MOF crystals based on dissolution of the parent framework followed by assembly of another type of framework was reported for a pillared paddle wheel framework [25]. These conversion approaches for MOF crystals are powerful tools for obtaining highly sophisticated functionalized frameworks; therefore, functionalities and fabrication of solid-solution frameworks are introduced after the synthesis of parent MOF crystals. However, these approaches have been limited to conversion between frameworks with the same or similar topologies in a crystalline-dispersed system. Hence, it is of great importance to develop an alternative approach to transform between frameworks with different topologies. In addition, the morphology control of the obtained crystals after conversion is a big challenge because the morphology of the MOF crystals significantly affects the properties of the frameworks because of its strong influence on the pore window size and shape of the exposed surface plane.

In this study, we propose a new strategy of a one-pot post-synthetic conversion between MOF crystals with different

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topologies on a two-dimensional substrate; it relies on sequential dissolution of parent MOF crystals and self-assembly of dissolved metal ions and organic ligands. The present simple approach for crystal conversion of MOF crystals can be applied to the conversion between the $[\text{Cu}_3(\text{btc})_2]_n$ (btc = 1,3,5-benzene tricarboxylate) framework with a twisted boracite topology and $[\text{Cu}_2(\text{ndc})_2(\text{dabco})]_n$ (ndc = 1,4-naphthalene dicarboxylate; dabco = 1,4-diaza bicyclo[2.2.2]octane) framework with a tetragonal topology (Scheme 1). This method provides a simpler fabrication process and offers a better opportunity for reversible conversion than crystal conversion in the dispersion system. Although an octahedral morphology is obtained for the resulting $[\text{Cu}_3(\text{btc})_2]_n$ crystals from an interfacial reaction using a metal ion-doped polymer substrate, cuboctahedral $[\text{Cu}_3(\text{btc})_2]_n$ crystals can be prepared using the present approach by changing the reaction solvent.

2. Experimental

2.1. Chemicals

Potassium hydroxide, copper acetate dihydrate, 1,4-naphthalenedicarboxylic acid, dabco, and 1,3,5-benzenetricarboxylic acid were purchased from Wako Chemicals, Ltd. Methanol, ethanol, and 1-butanol were purchased from Kanto Chemical, Ltd. All chemicals were used as received. Pyromellitic dianhydride oxydianiline-type polyimide films (50- μm thick, Kapton 200H, Du Pont-Toray Co., Ltd.) were used as polymer substrates. The films were cleaned prior to use by ultrasonication in ethanol at room temperature for 5 min.

2.2. Preparation of Cu^{2+} -doped polyimide films

The polyimide films ($1 \times 2 \text{ cm}^2$) were initially immersed in a 5-M aqueous KOH solution at 50°C for 5 min followed by thorough rinsing with copious amounts of distilled water. The modified films

were then immersed in a 100-mM aqueous $(\text{CH}_3\text{COO})_2\text{Cu}$ solution at room temperature for 20 min. After rinsing with distilled water, the ion-doped polymer films were immersed in a reaction solution containing organic ligands, followed by heating with microwave irradiation (Initiator+, Biotage).

2.3. Crystal conversion from $[\text{Cu}_3(\text{btc})_2]_n$ to $[\text{Cu}_2(\text{ndc})_2(\text{dabco})]_n$ frameworks

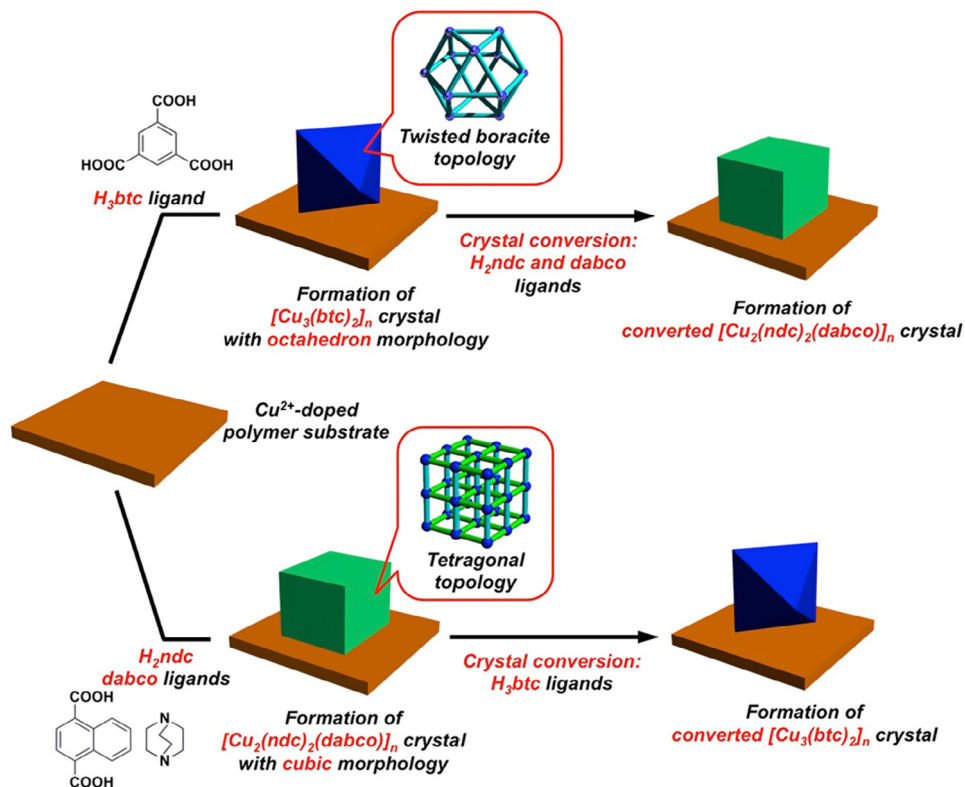
Cu^{2+} -doped polymer films were immersed into a methanol solution (5 mL) of 1,3,5-benzenetricarboxylic acid (10 mM), followed by heating at 150°C for 1 h with microwave irradiation. After rinsing with methanol, the obtained $[\text{Cu}_3(\text{btc})_2]_n$ crystals were then immersed into a methanol solution (5 mL) of 1,4-naphthalenedicarboxylic acid and dabco (10 and 5 mM, respectively), followed by heating at 150°C for 1 h with microwave irradiation.

2.4. Crystal conversion from $[\text{Cu}_2(\text{ndc})_2(\text{dabco})]_n$ to $[\text{Cu}_3(\text{btc})_2]_n$ frameworks

Cu^{2+} -doped polymer films were immersed into a methanol solution (5 mL) of 1,4-naphthalenedicarboxylic acid (H_2ndc) and dabco (10 and 5 mM, respectively), followed by heating at 150°C for 1 h with microwave irradiation. After rinsing with methanol, the obtained $[\text{Cu}_2(\text{ndc})_2(\text{dabco})]_n$ crystal films were then immersed into a methanol solution (5 mL) of 1,3,5-benzenetricarboxylic acid (H_3btc ; 10 mM), followed by heating at 150°C for 1 h with microwave irradiation.

2.5. Characterization

The surface morphology and thickness of the obtained MOF films were observed by scanning electron microscopy (SEM; JSM-



Scheme 1. Schematic representation of the proposed crystal conversion between $[\text{Cu}_3(\text{btc})_2]_n$ and $[\text{Cu}_2(\text{ndc})_2(\text{dabco})]_n$ crystals on a polymer substrate.

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