Synthesis of hydrogen-bonded organic frameworks based on a bis(benzimidazole)-coordinated zinc dichlorido complex using guest exchange

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Porous frameworks constructed through intermolecular hydrogen bonds are termed hydrogen-bonded organic frameworks (HOFs).[1] HOFs are mainly synthesized by recrystallization from solutions, including building block molecules; however, not all the solutions will give HOFs. For example, the crystallization solvents may prevent the building blocks from making the frameworks due to the formation of hydrogen bonds with the building blocks. Thus, methods for dealing with cases where HOFs are not obtained by recrystallization must be developed. In this presentation, with zinc complex **1** (Figure 1a),[2] we demonstrate that guest exchange, a process that replaces the guests in the porous frameworks with other molecules, is useful for converting non-HOF crystals to HOF.

When complex **1** was crystallized from *N*,*N*-dimethylformamide (DMF), DMF-solvated crystals ($\mathbf{1}_2$·$(DMF)_5$) were obtained (Figure 1b). A single crystal X-ray diffraction analysis of $\mathbf{1}_2$·$(DMF)_5$ revealed that the hydrogen bonding sites of **1** are all occupied by the N–H···O hydrogen bonds with DMF, and any framework via hydrogen bonds is not constructed. Thus, $\mathbf{1}_2$·$(DMF)_5$ can be concluded not to be a HOF. Next, $\mathbf{1}_2$·$(DMF)_5$ were exposed to acetone. As a result, a partial guest exchange proceeded to yield the crystals of **1**·$(acetone)_{0.5}(DMF)_{0.5}$ (Figure 1b). **1**·$(acetone)_{0.5}(DMF)_{0.5}$ has pores characterized predominantly by intermolecular N–H···Cl hydrogen bonds, proving the conversion of non-HOF crystals to HOF (Figure 1c). We will also report the results of exposing $\mathbf{1}_2$·$(DMF)_5$ to other organic vapors.

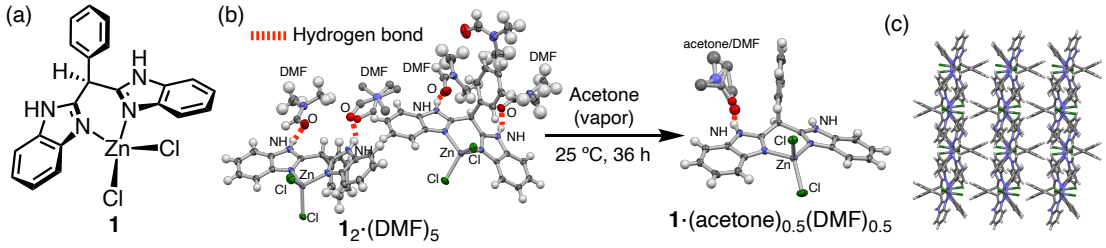

Figure 1. (a) Structure of **1**. (b) Conversion of $\mathbf{1}_2$·$(DMF)_5$ to **1**·$(acetone)_{0.5}(DMF)_{0.5}$. (c) 3D packing of **1**·$(acetone)_{0.5}(DMF)_{0.5}$.

1) I. Hisaki *et al., Angew. Chem., Int. Ed.* **2019**, *58*, 11160–11170. 2) S. Ohta *et al.*, *Inorg. Chem.* **2022**, *61*, 19890–19898.