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Short communication

Experimental study on interconversion between cubic MOF-5 and square MOF-2 arrays

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ABSTRACT

The synthesis of metal–organic frameworks (MOFs) often exhibits unpredictable complexity. Here, we report that MOF-5 formation at 120 °C takes a pathway different from the MOF-2-like crystal formation at 95 °C, and suggest that their interconversion requires degradation of the whole crystal structure.

Metal–organic frameworks (MOFs) are of great interest because of their porous structures [1–3], and have found numerous applications, for example, in gas storage [4], catalysis [5] or drug delivery [6]. Despite this popularity, the synthesis of MOFs composed of organic anionic linkers and inorganic knots often exhibits unpredictable complexity, resulting in production of various crystal phases with different porosity [7–10]. MOF-5, one of the most extensively studied MOFs with a nominal composition of $Zn_4O(BDC)_3$ [11] is no exception. MOF-5 contains 1,4-benzene dicarboxylate (BDC) linkers connected by six-handed octahedral knots (Scheme 1a, b). Reactions under subtly different conditions produce either MOF-2 ($[Zn(BDC)(H_2O)]DMF$) [12] or a compound with a nominal composition of Zn(BDC)(DMF) [13,14], which we call here MOF-2-DMF. These compounds are composed of two-dimensional (2-D) sheet arrays of squares assembled through planar four-handed knots (Scheme 1b). While the diversity of the reactions centered around a mixture of BDC, $Zn(NO_3)_2{\bullet}6H_2O$, water and DMF has recently been summarized [15,16], and it has been reported that the pH can determine the formation of MOF-2-DMF or MOF-5 [17], the correlation between these two structures has so far received scant attention, possibly because of the seemingly obvious structural similarity. In this article, we report that such similarity is deceptive and that MOF-5 formation takes a pathway different from MOF-2 formation. Considering the structural dissimilarity of the four- and six-handed knots, their interconversion requires degradation of the whole crystal structure into small assemblies similar to prenucleation clusters formed at the very beginning of MOF crystal formation. However, interconversion of MOF-2-DMF and MOF-2 occurs readily because it needs mere removal or addition of water molecules. The present analysis of the knot structure suggests that the presence of an acetate ion (capping effect) facilitates the formation of MOF-5 and MOF-2 from $Zn(OAc)_2{\bullet}2H_2O$ in DMF or water/DMF mixture.

MOF-5 with a 3-D cubic lattice was synthesized following the literature procedure [7], by heating a mixture of 1 equiv. of H_2BDC and 2 equiv. of $Zn(NO_3)_2{\bullet}6H_2O$ in DMF at 120 °C overnight (Fig. 1a, b). Here, we made an interesting observation that has apparently escaped the notice of MOF researchers: When the reaction temperature was lowered by 25 °C, the reaction produced MOF-2-DMF crystals (Fig. 1c, d). According to the literature, when MOF-2-DMF is placed in moist air, the four-handed knots are hydrated by water molecules to create pores among the 2-D square arrays to form MOF-2 [13]. In a vacuum, MOF-2 loses water molecules to regenerate MOF-2-DMF. As seen from the published crystal structures, this interconversion does not change the geometry of the 2-D square array much.

Therefore, we became interested in the structural correlation between MOF-5 and MOF-2-DMF/MOF-2, which were formed under very similar reaction conditions. Apparently, their knots are structurally different and appear hardly interconvertible with each other (Scheme 1b). The six-handed knot in MOF-5 has a dianionic oxygen coordinated to four Zn(II) atoms, while the four-handed knot in MOF-2 contains two carboxylate units $[Zn(OCOR)_2]_2$. We found that treatment of pure MOF-2-DMF or MOF-2 in DMF at 120 °C with ~1 equiv. $Zn(NO_3)_2{\bullet}6H_2O$ afforded exclusively MOF-5 crystals, as confirmed by PXRD analysis, because, at such high temperature, the water molecules react with zinc forming ZnO. However, heating MOF-2-DMF or MOF-2 in DMF without

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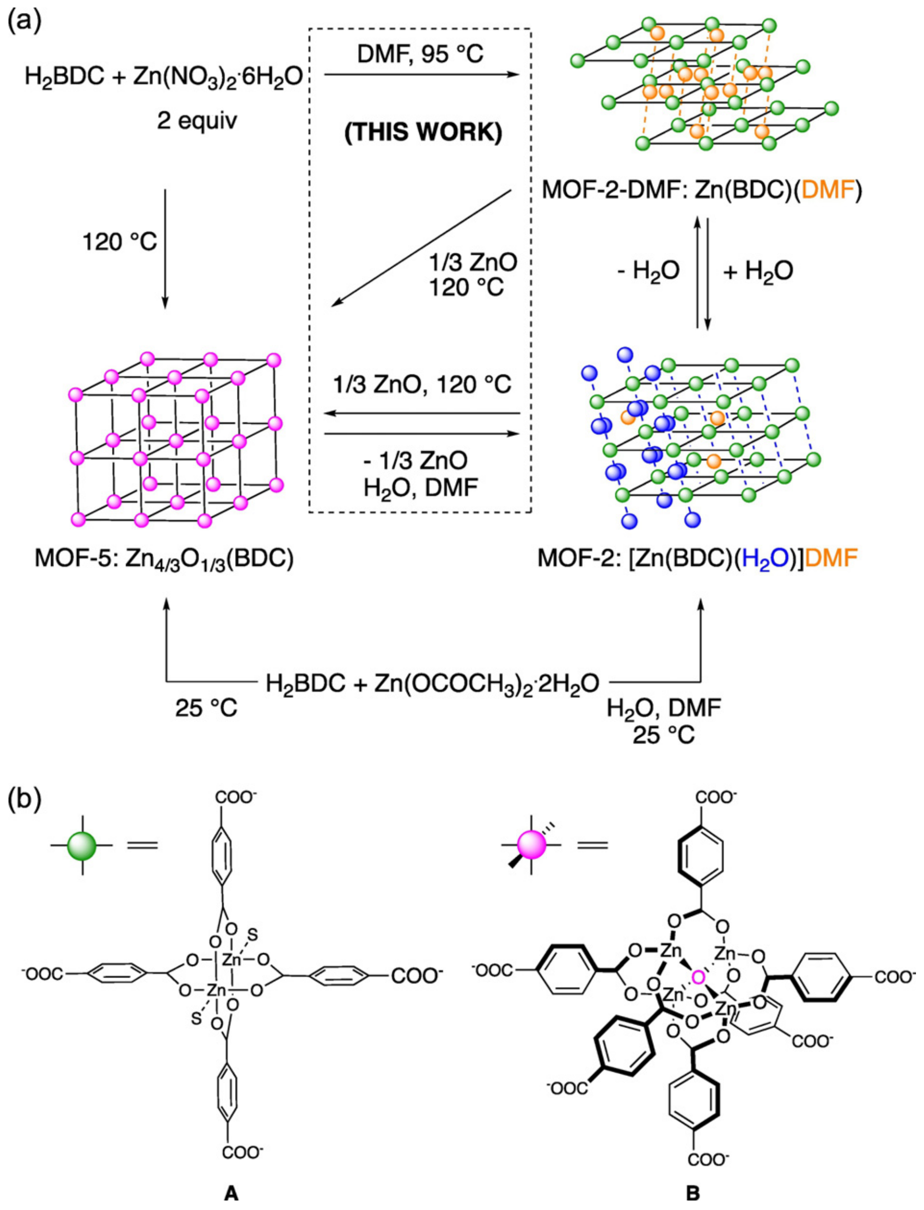

Scheme 1. (a) Structural relationship between MOF-2-DMF, MOF-2 and MOF-5; (b) Four-handed knot (left, S = solvent) and six-handed octahedral knot (right).

$Zn(NO_3)_2$•$6H_2O$ produced a mixture of MOF-2-DMF and MOF-5. Conversely, we found that removal of the basic ZnO component from the six-handed knot by the addition of aqueous HCl to MOF-5 in DMF readily produced MOF-2 (Scheme 2).

The four-handed knot creates 2-D square arrays and the six-handed knot creates 3-D cubic arrays, where the fast-growing 2-D network should be a kinetic product as suggested by recent molecular dynamics calculation [20] and the 3-D structure should be a thermodynamic product. The above experiments are consistent with the transformation expected for MOF-5 and MOF-2 in which ZnO addition is necessary for the conversion of the four-handed knot to the six-handed knot, and removal of ZnO by HCl is needed for the reverse transformation. Here, it is proposed that the conversion of MOF-2 to MOF-5 or vice versa requires structural changes so large that it must accompany disintegration of the crystal lattice into small fragments similar to nm-sized mobile prenucleation clusters generated at the beginning of the MOF crystal formation. There have been no experimental studies on the structure of such clusters to date, while the theoretical simulations on the prenucleation cluster of MOF-2 formation may provide some hints about their structures and behavior [20]. Our attempts to detect minute PNCs by dynamic light scattering (DLS) analysis of DMF during MOF-2 to MOF-5 conversion (30 min to 12 h after constant heating) failed to show any signals due to nm-sized objects, suggesting that the concentration of PNCs is below detection limit of DLS (0.5 mg/mL).

The nature of the anionic ligand on the zinc(II) atoms and the coordination geometry are expected to affect the disintegration/integration processes greatly. On the one hand, as depicted in Scheme 3a on the basis of reported theoretical simulations [20], the nitrate anion in the standard MOF-2 and MOF-5 synthesis is only weakly bound to a zinc knot intermediate, and hence would readily dissociate to form preferentially a linear knot for steric or Coulombic reasons. On the other hand, the corresponding knot intermediate made from $Zn(OAc)_2$ (Scheme 3b) would be more prone to make an angular knot suitable for participating in the formation of a square (C) or a cube (D). Such a role of added carboxylate anion has been known as capping and is of significant importance for the promotion of ligands for self-assembly [21]. In accordance with this capping concept, MOF-5 can be synthesized from zinc acetate dihydrate at room temperature within only