



# Metal-organic framework engineering: directed assembly from molecules to spherical agglomerates



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## ABSTRACT

[In(OH)(bdc)]<sub>n</sub> (bdc = 1,4-benzenedicarboxylate) was used as the model metal-organic framework for showing the concept of directed assembly from molecules to spherical agglomerates in solution. The course of reaction crystallization at 60°, 80° and 100 °C could be partially fulfilled by the Avrami equation. Noticeably, the portion which failed to be fitted by the equation was the secondary crystallization. Aging and editing effects during the course of secondary crystallization were responsible for the increase in crystallinity and structural rearrangements of [In(OH)(bdc)]<sub>n</sub> crystals. The spherical agglomerates of [In(OH)(bdc)]<sub>n</sub> crystals were assembled by the liquid bridges among the [In(OH)(bdc)]<sub>n</sub> crystals through the addition of a polyethylene glycol (PEG) binder. The growth of spherical agglomerates was traced and described by three curves: the depletion curve, the reaction progress curve, and the average agglomerate size versus mixing time curve.

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## 1. Introduction

Metal-organic framework (MOF), or porous coordination polymer (PCP), is a hybrid crystal formed by the connection of either inorganic single metal centers or clusters and organic linkers [1]. The many different combinations of those building blocks and the readiness of them to be functionalized [2] have offered MOF some unique chemical versatility with a designable framework and inner porosity [3]. Analogous to enzymes with specific topography and binding sites comprising metal atoms [4], MOFs have applications in many diverse areas such as gas storage [5] and separation [6], drug delivery [7], bio-imaging [8], catalysis [9], and chemical sensing [10]. Interestingly, the supramolecular coordination complexes and the permanent porosity in MOF can sometimes lead to a wide range of emissive phenomena via their luminophores [11]. Given with all those fascinating properties [12], most of the studies are focusing on the discovery [13], novel preparation methods [14] and functional applications of MOF [5–10,15].

However, morphological issues of MOF crystals, such as solid-state phase, particle size distribution, porosity and sphericity, could have profound effects on their stability, flowability, packability and photoluminescence in the downstream process and their end-use [16]. For instance, spherical MOF crystals with high flowability and packability could increase their compaction and packing efficiency in a vessel, which could significantly affect their volumetric and

gravimetric uptake of methane from natural gas [5c] during storage and delivery [17]. Many industrial applications of MOF, such as catalysis, extraction, drug delivery and sensing, may also count on the reproducibility of MOF's structural stability, pore size, pore surface area and photoluminescent performance [18]. Consequently, the directed assembly of MOF from molecules to spherical agglomerates should be understood in details. The crystallization of MOF is generally carried out by an irreversible reaction in dimethylformamide (DMF) or other common organic solvents in which MOF crystals are slightly soluble. Once MOF molecules are assembled and precipitated out as crystals, structural editing of MOF afterwards is difficult to achieve by dissolution-and-re-crystallization. On the other hand, a spherical agglomeration technique of producing round particles [19,20] *in situ* by the assembly of primary crystals [21] has been available for a long while.

Noticeably, synthesis of MOF crystals in a gram-scale or larger scale is surprisingly rare [22]. So far, only a small number of investigations have concerned with the kinetics [23] and process parameters [24] in a milligram-scale with the absence of transport phenomena [25]. Only the crystallinity of MOF crystals were monitored by solid-state characterization tools such as small-angle X-ray scattering (SAXS) [26], powder X-ray diffraction (PXRD) [27] time-resolved light scattering (TLS) [28], surface plasmon resonance (SPR) [29], and atomic force microscopy (AFM) [30], even though many indications have pointed to the importance of tracing some other structural variables such as porosity [31].

Therefore, the aim of this paper is to make use of [In(OH)(bdc)]<sub>n</sub> (bdc = 1,4-benzenedicarboxylate) [15,32] also

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known as In-MIL-68 [33] to study the assembly of MOF from molecules to spherical agglomerates in a gram-scale. In general,  $[\text{In}(\text{OH})(\text{bdc})]_n$  crystals were synthesized by reacting indium salt (metal) with 1,4-benzenedicarboxylic acid (ligand) via the solvothermal process. The effects of solvent, indium precursors, salt hydration, metal:ligand ratio and solid loading in a milligram-scale on MOF production would be screened initially by polarized optical microscopy (POM), infrared spectroscopy (IR) and PXRD for determining a reliable operating landscape [24]. Then, the effects of time and temperature for reaction crystallization on nucleation and crystal growth of MOF, and the influence of particle loading for spherical crystallization on crystallinity, particle size and pore size distribution, and photoluminescence of MOF, would be investigated all together.

Although we did not have any *in-situ* sensors such as the attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectroscopy for accurate determination of the solute concentration, the focused beam reflectance measurement (FBRM) for particle size distribution, and the process vision and measurement (PVM) for video microscopy [34], the problems were overcome by *in-line* analytical substitutes such as the thermocouple for recording the reaction temperature, ultraviolet and visible (UV/vis) spectrophotometry for determining the ligand concentration, and optical microscopy (OM) and scanning electron microscopy (SEM) for observing the crystal habits. Those techniques are easy to access and can be coupled with other *off-line* solid-state characterization methods, such as PXRD, dry sieving method, the Carr's index, nitrogen adsorption, helium pycnometry, mercury intrusion porosimetry (MIP), and photoluminescence (PL) spectrophotometry, for monitoring the impact of the assembled structures on the properties of MOF, and thus giving some important information for process control in the future.

## 2. Experimental section

### 2.1. Kinetics studies

1.95 g of (6.5 mmol)  $\text{In}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$  were dissolved in a 20 ml scintillation vial containing 15 ml of DMF. 0.75 g of (4.5 mmol)  $\text{H}_2\text{bdc}$  was dissolved separately in a 350 ml three-neck round bottom flask filled with 185 ml of DMF. The middle neck of the flask was connected to a Dimroth condenser for reflux. The right neck was plugged by a silicon rubber stopper inserted with a syringe needle for sampling. The resulting solutions in the vial and the round bottom flask under agitation at 300 rpm were heated together to 60 °C, 80 °C or 100 °C in an oil bath before mixing. At the instant of mixing, the  $\text{In}(\text{NO}_3)_3$ -DMF solution in the vial was introduced rapidly into the  $\text{H}_2\text{bdc}$ -DMF solution in the round bottom flask to form a 200 ml reaction medium and the time was set to  $t = 0$  h. At a regular time interval, 0.5 ml of slurry was withdrawn by a syringe and centrifuged. 0.2 ml of the supernatant was then diluted 50 times with DMF before determining its concentration by UV-vis spectrophotometry. Once the absorbance value had ceased to drop indicating the reaction was finished, the slurry was cooled to room temperature gradually along with the oil bath. The slurry was filtered. The wet cake was rinsed with DMF three times and oven dried at 40 °C overnight to give the as-synthesized solids. The samples were then characterized by TGA as shown in Fig. S1a. DMF was completely removed after 200 °C and MOF began to decompose after 450 °C. Therefore, the as-synthesized solids were vacuum oven dried at 250 °C for 12 h to desolvate the DMF in the crystal lattice.

### 2.2. Spherical agglomeration

$[\text{In}(\text{OH})(\text{bdc})]_n$  crystals synthesized at 100 °C would be used for all spherical agglomeration experiments because the reaction

crystallization time required was the shortest compared with the ones of the syntheses at 60 ° and 80 °C. Since  $[\text{In}(\text{OH})(\text{bdc})]_n$  crystals were sparingly soluble in common organic solvents, it was hard to find a solvent to act as a bridging liquid [35]. To overcome this problem, a common binder, *polyethylene glycol* (PEG), was used [21d]. The ethanolic PEG solution was employed to coagulate the  $[\text{In}(\text{OH})(\text{bdc})]_n$  crystals through the formation of liquid bridges among MOF crystals.

1 g of as-synthesized  $[\text{In}(\text{OH})(\text{bdc})]_n$  crystals was suspended in 300 ml of *n*-heptane, stirred at 500 rpm and kept at 25 °C. 3.2 ml of 50 wt% of PEG-ethanol solution as a binding liquid was added dropwise to the MOF suspension at a rate of 0.2 ml/min. However, the volume of the binding liquid was increased to 11 ml for a 5 g loading of as-synthesized  $[\text{In}(\text{OH})(\text{bdc})]_n$  crystals. A small amount of suspension was withdrawn from time to time for OM examination. After 4 h of stirring, the slurry was filtered and the spherical agglomerates were oven dried at 40 °C overnight. The TGA scan of PEG in Fig. S1b showed that PEG started to degrade after 150 °C, and the TGA scan of  $[\text{In}(\text{OH})(\text{bdc})]_n$  spherical agglomerates in Fig. S1c further suggested that the weight loss between 50 ° and 150 °C was due to the removal of ethanol. Therefore, the spherical agglomerates with PEG were vacuumed dried at 150 °C for 12 h to avoid the decomposition of PEG.

### 2.3. Vapor sensing

10 mg of 250 °C vacuum dried  $[\text{In}(\text{OH})(\text{bdc})]_n$  crystals or 150 °C vacuumed dried spherical agglomerates were placed in a 7 ml open scintillation vial which was placed inside a 100 ml sealed bottle containing about 3 ml of *p*-xylene. The whole system was kept at 40 °C for 6–8 h. PL spectra of the samples were then collected and analyzed.

### 2.4. The Carr's index

The Carr's index,  $C$ , is defined as:

$$C = \frac{\rho_t - \rho_p}{\rho_t} \times 100\%$$

where the poured density,  $\rho_p$  = the mass of the sample powders divided by the undisturbed volume of 1 g of sample right after filling in a 10 ml graduated cylinder, the tapped density,  $\rho_t$  = the mass of the sample powders divided by the powder volume after tapping the graduated cylinder 200 times until no more change in the powder volume was observed. The Carr's index was used for measuring the powder flowability.

### 2.5. Dry sieving method

About 1 g of 40 °C oven dried spherical agglomerates was introduced to the top of a stack of metal sieve plates organized from the largest to the finest aperture in the order of 1000, 710, 500, 297, 250, 149, 125, 74  $\mu\text{m}$  (Kuang Yang, Taiwan) for the determination of the particle size distribution of spherical agglomerates. Each sieve was slightly tapped with a spatula on the side to enhance powder flow. Sieves with the retained spherical agglomerates were imaged by OM. The weight % of each size cut was obtained by dividing the weight of spherical agglomerates on a particular sieve plate with the total weight of spherical agglomerates on all sieve plates.

## 3. Results and discussion

### 3.1. Reaction and crystallization

Six synthesis parameters: (1) solvent, (2) metal salt, (3) metal:ligand ratio, (4) hydration, (5) solvent volume reduction, (6) time

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