### Article

# Porous Crystalline Spherulite Superstructures



We report the fabrication of metal-organic framework (MOF) spherulite superstructures based on an unconventional small-angle branching mechanism. These superstructures are constructed from bottom-up assembly of MOF nanorod crystallites via a facile solvothermal synthesis and exhibit a "Maltese cross" extinction pattern typical of spherulites under a polarized light. This work provides approaches to packing porous crystallites and fabricating sophisticated superstructures, which are expected to serve applications from catalysis to guest delivery and transportation. Liang Feng, Kun-Yu Wang, Tian-Hao Yan, Hong-Cai Zhou

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#### HIGHLIGHTS

Porous spherulites are observed with a "Maltese cross" pattern under a polarized light

Simple solvothermal synthesis leads to sophisticated spherulite superstructures

Evolution involves an unconventional small-angle branching mechanism during MOF growth

Mechanistic effects of solvent decomposition kinetics on the evolution are revealed



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### Article

# Porous Crystalline Spherulite Superstructures

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#### **SUMMARY**

Assembly of crystallites into three-dimensional hierarchical superstructures is vital for the design of multicomponent architectures as capsules and reactors for storage, delivery, and catalysis. However, the development of these assemblies, for example, spherulite superstructures, has mainly been hampered by limited control over nucleation, orientational growth, and stability. In this work, we observed a hierarchical evolution from metal-organic framework (MOF) nanofibrils into spherulite superstructures. Under a polarized light, these superstructures exhibited a "Maltese cross" extinction pattern typical of spherulites, which is the first time this has been observed in porous materials. We demonstrated that by tuning the evolution kinetics via a mixed-solvent approach, varying morphologies could be obtained as a result of small-angle branching. Isoreticular expansion of MOF spherulites and incorporation of multiple components could also be achieved. This work provides a fresh avenue to pack porous crystallites into sophisticated superstructures, which are expected to serve applications from catalysis to guest delivery and transportation.

#### INTRODUCTION

Evolution of crystallites into hierarchical superstructures is critical for the design of multicomponent architectures as capsules and reactors for storage, delivery, and catalysis.<sup>1</sup> Spherulite superstructures refer to radially polycrystalline aggregates with an external spherical envelope, which has been widely observed in crystallization processes of polymers, metals, minerals, and inorganic crystals.<sup>2-9</sup> For instance, rod-like cellulose crystallites are regulated to lie along the radius or along the circumference to form spherulites.<sup>2</sup> Some proteins can also be self-associated into high-order spherical structures.<sup>8</sup> The fundamental characteristics of spherulites have mainly been deduced by a typical "Maltese cross" pattern of light extinction from polarized light microscopy. For example, the spherulite crystallization of insulin, a highly flexible polypeptide system, could be observed by polarized optical microscopy, while the Maltese cross extinction pattern disappeared after drying and rehydration, indicating the fragile nature of protein spherulite structures.<sup>8</sup> Additionally, inorganic minerals including alkaline feldspars, plagioclase, chalcedony, and malachite have been widely found, both in laboratory and in nature, in the form of spherulite superstructures.<sup>2</sup>

Strangely, the evolution of spherulite superstructures from porous materials including metal-organic frameworks (MOFs), zeolites, porous carbon, or silica has not been widely explored yet, given the rapid progress in the self-assembled spherulite of metals, polymers, proteins, and other materials. MOFs are a class of porous crystalline materials assembled from organic linkers and inorganic clusters.<sup>10–14</sup> The intrinsic tunability over pore environments promises MOF's wide applications

#### **The Bigger Picture**

Spherulites are radially polycrystalline aggregates with an external spherical envelope. The hierarchical assembly of sophisticated spherulites architectures is a ubiquitous phenomenon in nature, such as in polymers, metals, minerals, and inorganic crystals. However, further exploring the assembly process in porous materials and uncovering the mechanisms remain a sustainable challenge. Here, we present an unprecedented case of metalorganic framework (MOF) spherulite assembly by carefully controlling solvent decomposition, spherulite nucleation, and directional growth. Instead of traditionally observed MOF single crystals, porous spherulite superstructures with well-organized crystallites and tunable pore environments were obtained after solvothermal reaction. This research exhibits the beauty of porous hierarchical superstructures and also provides a synthetic approach to pack porous crystallites into sophisticated superstructures for catalysis, delivery, and transportation.

including storage, separation, catalysis, and sensing.<sup>15–19</sup> So far, only a few studies have illustrated the potential to fabricate porous spherical MOF superstructures.<sup>14,20,21</sup> For instance, Maspoch and co-workers reported a spray-drying strategy for the synthesis of spherical hollow superstructures. These hierarchical assemblies enable the encapsulation of guest species and can function as reactors for delivery and catalysis.<sup>22</sup> Xu and co-workers also reported a chestnut-shell-like MOF-74(Zn) spherical superstructure composed of MOF nanorods on the shell formed under hydrothermal conditions with urea as a modulator.<sup>23</sup>

The development of porous self-assembled spherulite superstructures has mainly been precluded by limited control over nucleation, directional growth, and framework stability. In this work, we describe the observation and mechanism study of MOF spherulite superstructures assembled through evolution of MOF nanofibrils. To the best of our knowledge, this is the first time that an optical Maltese cross pattern was observed in the porous material world including MOFs, zeolites, and others. The formation of MOF spherulites is further characterized and studied by optical microscopy, scanning electron microscopy (SEM), and transmission electron microscopy (TEM). We demonstrate that the resulting compact MOF spherulite architectures are assembled from fibrous crystallites, which further undergo Ostwald ripening to make interface coarsened. This work provides a fresh avenue to pack porous crystallites and fabricate porous sophisticated superstructures, which are expected to serve applications from catalysis to transportation.

Our findings originated from our previous studies into MOF-74-II (Figures S1–S5).<sup>24</sup> Due to the existing open metal sites along its 1D channels, MOF-74 shows great potential in gas storage, separation, and catalysis.<sup>25-28</sup> It should be noted that varying reaction conditions of MOF-74 can generate diverse morphology evolution behaviors. For example, Dai and co-workers demonstrated the template-free synthesis of hierarchically porous MOF-74 by etching the framework with various solvents for different periods.<sup>29</sup> Xu group also observed the formation of superlong single-crystal Co-MOF-74 nanotubes with a diameter of  ${\sim}70$  nm and length of 20–35  $\mu$ m through a recrystallization approach.<sup>30</sup> In addition, Zn-MOF-74 could also be prepared directly from a metal oxide without bulk solvent through mechanochemistry.<sup>31</sup> More interestingly, Zhou group recently discovered a temperature-controlled evolution from MOF-74 crystallites to hierarchically porous superstructures including single-crystalline hollow tubes, ripened hierarchically porous multichannel tubes or helical tubular structures. It was found that N,N-diethylformamide (DEF) solvent could decompose slowly under solvothermal conditions, modulating the assembly of these superstructures.

#### RESULTS

#### Self-Assembly of Porous Crystalline MOF-74-III Spherulite Superstructures

Herein, we judiciously choose N,N-dimethylformamide (DMF) solvent as the reaction medium to accelerate the assembly of hierarchical superstructures. Strikingly, the reaction of zinc nitrate and organic linker III in a mixture of DMF, ethanol, and water by conventional solvothermal conditions yields colorless MOF-74-III spherulites within a few hours (Figure 1A). MOF-74-III contains one-dimensional hexagonal channels with a channel size of about 2.9 nm, and powder X-ray diffraction (PXRD) patterns indicate its phase purity (Figure S8A). Nitrogen sorption experiments on the MOF-74-III verify its mesoporosity (Figure S17). Optical microscopy reveals that the materials consist of spherical particles ranging in size from around 20 to

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#### Figure 1. Discovery of Hierarchical MOF-74-III Spherulite Superstructures

#### (A) Optical images of MOF-74-III spherulites.

(B) SEM images showing that MOF-74-III spherulites contain a large number of well-defined fibrils. (C and D) Optical image and the corresponding polarized optical images of MOF-74-III spherulites placed in between crossed polarizers. The image displays a typical Maltese cross extinction pattern indicating spherulite superstructures under a polarized light.

(E) TEM images of a typical MOF-74-III spherulite showing the fibril size and arrangement.

(F) TEM images of a peanut-like MOF-74-III spherulite showing the fibril size and arrangement. Scale bar, 100 µm in (A), (C), and (D), 5 µm in (B), and 250 nm in (E) and (F).

40  $\mu$ m (Figure S10). Surprisingly, the resulting material MOF-74-III displays a clear Maltese cross extinction pattern typical of spherulite superstructures under a polarized light (Figures 1C and 1D), which has never been seen in previous reports regarding porous materials, to the best of our knowledge. This Maltese cross pattern consists of four dark perpendicular cones diverging from the bright spherulite center and colored brighter regions in between them (Figure 1D).

As the MOF-74-III particles were air-dried under the optical microscope, the spherulites were observed to maintain its hierarchical structure, although partial deformation was observed on some particles as indicated by the cracks caused by the fragile superstructures (Figures S6 and S7). Ultimately, the Maltese cross pattern disappeared once the solvents were totally released. However, infusion of the sample back into DMF could reestablish the Maltese cross extinction pattern, indicating the robustness of the framework and the overall hierarchical spherulite structure (Figures S6 and S7).

The morphology of MOF-74-III was also imaged by field-emission scanning electron microscopy (FESEM, Figure 1B). It was found that a high density of individual MOF-74-III fibers with almost identical lengths and sizes were arranged to form a sphere. The MOF-74-III crystallites are elongated along a principal axis of the optical indicatrix, leading to a Maltese cross extinction between crossed polarizers. Notably, there are discretely distributed spheres, peanut-like spherulites, and spherulites consisting of multiple spheres found as the crystallization products, depending on the nucleation position and growth rates of a specific spherulite (Figures 1C and S9–S12). The well-aligned crystallites outside hierarchical MOF-74-III spherulites were further confirmed by regular TEM (Figures 1E and 1F). As indicated by TEM images, the spherulites contain a large number of well-defined fibrils ranging in diameter

from around 40 to 60 nm, suggesting that the spherulites are assembled from MOF nanofibrils.

#### Spherulite Superstructure Evolution Mechanism

To study the evolution behavior of MOF-74-III spherulites, the solvothermal reaction products at different periods were monitored (Figures 2B–2G). We observed that initial spherulites around 15  $\mu$ m in diameter formed within 3 h (Figure 2C). After a 6 h reaction time, continuous epitaxial growth of the MOF fibers with around 30  $\mu$ m diameter was observed (Figure 2E). As the reaction time further extended, the sizes of MOF-74-III spherulites remained almost unchanged, which indicated the completeness of MOF growth process (Figures 2F and 2G).

In most cases, crystal growth from a typical primary nucleus into a crystallite exhibits a discrete crystallographic orientation, producing a single crystal with well-defined shapes and morphology as a product (Scheme 1A). Yet, there are certain systems that are unable to grow in a discrete crystallographic orientation and form a single crystal, for example, spherulites. The growth of spherulites involves the branching of fiber crystallites, where the crystallographic orientation of individual crystallites deviates slightly from that of its parent fiber (Scheme 1B). As a result, a radiating array of crystalline fibers was formed as spherulites. Notably, the formation of spherulites has been observed in a diverse library of materials including polymer, inorganic salts, metals, and other materials. The similar morphology and spherulitic crystallization behaviors in these materials suggest a possible general mechanism regardless of their molecular compositions. As suggested by previous reports,<sup>2,32</sup> due to the occurrence of the small-angle branching and associated radial growth, spherulites consisting of radial and dense fibers are formed. Uniform radial growth on MOF-74-III nuclei could continue in all directions, while further secondary crystallization associated with lateral growth or coarsening of MOF fibers proceeds subsequently (Figure 2B).

As indicated by the FESEM images of fractured spherulites, the lateral interfaces among individual crystallites were coarsened via highly reversible coordination bond formation and reconstruction and then proceeded to form a united superstructure (Figures 2A–2H). This has also been observed in the previous report and can be explained by a coarsening mechanism.<sup>33–36</sup> Since MOF-74-III crystallites grow close to each other, the restricted assembly would contribute to transform the pre-aligned needle-like crystallites into a dense MOF sphere via Ostwald ripening, resulting in a robust isolated spherulite.

We further demonstrate that by tuning the kinetics of superstructure evolution via a mixed-solvent approach, varying morphologies can be obtained (Figures 3 and S13). It is realized that regulating the growth rate of crystallites is extremely important for the formation of spherulite superstructures. By tuning the ratio between two solvents with different decomposition rates, namely DMF and DEF, during the superstructure evolution, the growth rate of MOF-74-III crystallites and the spherulite states could be controlled. At higher DEF ratios, the slow release of diethylamine as the DEF decomposition product could induce the slow deprotonation of linker III and growth of MOF-74-III crystallites. As a result, needle aggregates were obtained while no spherulites could be discerned (Figures 3C, 3G, and 3H). The aggregates were relatively fragile and became individual needle crystals upon a sonicated treatment.

Conversely, at higher DMF ratios, the release of diethylamine was accelerated, ultimately leading to the fast epitaxial growth of MOF-74-III crystallites in all directions and then the formation of spherulites (Figures 3A, 3D, and 3E). It should be noticed





#### Figure 2. Mechanism Study on Spherulite Superstructure Evolution

(A) Illustration of lateral coarsening between neighboring crystallites, which leads to the formation of a fused core inside MOF-74 spherulites.

(B) Illustration of epitaxial growth of MOF-74 spherulites with 1D channels.

(C–G) Optical image and the corresponding polarized optical images of MOF-74-III spherulites placed in between crossed polarizers showing the time-dependent superstructure evolution process: (C) 3 h, (D) 4.5 h, (E) 6 h, (F) 8 h, and (G) 24 h.

(H) The structural mode of MOF-74 spherulites with surface fibrils and a fused core.

(I) SEM images showing well-defined fibrils on the surface of a spherulite and a fused core inside the spherulite.

(J–L) SEM images of cracked MOF-74 spherulites; the optical image of a cracked MOF-74 spherulite was inserted in (L). Destruction methods such as cutting and ultrasound treatment were conducted to unveil the interior morphology information of spherulites. Scale bar, 100  $\mu$ m in (C–G) and (I–L).



#### Branching: Orientation of Individual Crystallites Deviates

#### Scheme 1. Growth Habits of Traditional Single Crystals and Spherulites

that we did not observe the presence of MOF fibrils in the sonicated solutions, which indicated the lateral coarsening between the MOF crystals. As indicated by SEM images of partially damaged spherulite samples, MOF-74-III spherulites with surface fibrils and a fused core were clearly observed (Figure 2H). The SEM images of cracked MOF-74 spherulites also revealed the internal fused core without distinguishable fibril structures observed in the core (Figures 2J-2L and S12). These results suggest that the noncore regions of these superstructures consist of radially arranged fibrils, while the core fibrils undergo orientational assembly and coarsening processes. Interestingly, we captured the intermediate state between needle aggregates and spherulites when DMF/DEF (1:1) solvents were mixed to induce the formation of MOF-74 spherulites. The resulting sphere structure was mainly consisted of fibril crystallites, which could be observed in the optical images, while a weak Maltese cross extinction pattern was still observed (Figures 3B and 3F). The results of this study therefore provide enhanced understanding of the assembly process that fabricates from mesoporous MOF fibrils to hierarchical spherulite superstructures, which shall be vital for their exploitation as sophisticated porous materials and in nanotechnology.

#### **Isoreticular Synthesis of MOF-74 Spherulites**

One well-known facet of MOF-74 is that the pore size can be systematically expanded by elongating the linker length.<sup>28,37</sup> We inferred that superstructures with isoreticular MOFs could also be assembled by simply tuning the organic linker lengths under similar conditions. To this end, we utilized linker II and IV to construct isoreticular MOF-74-II and MOF-74-IV with 2.2 and 3.5 nm hexagonal channels, respectively (Figures 4A–4C). Experimental observations confirmed that both MOF spherulite superstructures could be obtained (Figures 4D–4F and S9–S11). PXRD patterns of MOF-74-II and MOF-74-IV indicated their phase purities, and optical microscopy revealed that the materials displayed a clear Maltese cross extinction pattern, demonstrating the successful preparation of MOF-74 spherulite superstructures (Figures S9–S11 and 4D–4F). This unique observation demonstrates that the porosity of MOF superstructures can be readily tuned without altering overall arrangement of the crystallites.

#### **Introducing Multiple Components into MOF-74 Spherulites**

The highly tunable synthesis of porous crystalline spherulites enables the fabrication of multicomponent MOF superstructures (Figure 5). To explore the possibility, a small amount of  $Co(NO_3)_2.6H_2O$  was incorporated into the precursors of MOF-74-III

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#### Figure 3. Tuning the Kinetics of Superstructure Evolution by a Mixed-Solvent Approach

(A–C) Structural illustration of superstructures during MOF-74 growth in mixed DMF/DEF solvent environments, (A) fast growth of MOF-74 in DMF solvents leads to the formation of spherulites with surface fibrils and a fused core, (B) superstructures with assembled fibrils and a weak Maltese cross extinction pattern were observed due to the moderate growth of MOF-74 in DMF/DEF (1:1) solvents, and (C) superstructures assembled from large needle crystallites can be obtained after the solvothermal reaction in DEF solvents.

(D–H) Optical images and the corresponding polarized optical images showing diverse morphologies obtained by mixing DMF and DEF in varying ratios (DMF/DEF, mL/mL), (D) 2: 0, (E) 1.5: 0.5, (F) 1: 1, (G) 0.5: 1.5, and (H) 0: 2. Note that some fibril fragments can be observed in the inserted images of (F), highlighted by the arrows. Scale bar, 100  $\mu$ m in (D–H).

(Zn) before the formation of MOF spherulites. After the reaction, bimetallic MOF spherulites could be fabricated with a clear Maltese cross extinction pattern (Figure S14). The energy dispersive X-ray (EDX) elemental mapping indicated the well-mixed nature of Zn and Co ions in the superstructures (Figure S14). Further incorporating multiple metal ions including  $Zn^{2+}$ ,  $Co^{2+}$ , and  $Ni^{2+}$  into MOF-74-III spherulites was conducted (Figures 5A and 5B). The phase purity was confirmed by the PXRD pattern of the corresponding MOF-74 (Figure S8). Optical images and SEM-EDX analysis showed the well-maintained spherulite superstructure, and the metal composition was analyzed by ICP-MS, showing 92.0% Zn, 2.6% Ni, and 5.4% Co dispersed in the hierarchical structure (Figures 5A and 5B). Additionally, the incorporation of functional organic components into these frameworks provides a facile route to prepare stable, multivariate, and hierarchical materials.<sup>15,18</sup> For example, doping a small amount of catalytically active ligands such as metal phthalocyanine Co[Pc(COOH)<sub>4</sub>] into the hierarchical MOF-74-III superstructures could also be achieved without interrupting the formation of spherulites (Figure 5C).

The hierarchically porous superstructures of MOF-74 spherulites provide a unique mesoscopic environment for guest storage and delivery. We further illustrated that MOF-74-III spherulites could be utilized for dye capture (Figure 5D). Post-synthetic encapsulation of



#### Figure 4. Isoreticular Synthesis of MOF-74 Spherulites with Tunable Pore Sizes

(A–C) Shown is a structural illustration of MOF-74-II, III, IV, and their assembled spherulite superstructures, : (A) MOF-74-II with 2.2-nm intrinsic channels,
(B) MOF-74-III with 2.9-nm intrinsic channels, and (C) MOF-74-IV with 3.5-nm intrinsic channels.
(D–F) Optical images and the corresponding polarized optical images showing the spherulite morphology of (D) MOF-74-II, (E) MOF-74-III, and (F) MOF-74-IV. Scale bar, 100 μm in (D)–(F).

an organic dye (methylene blue) into the mesoporous channels of MOF-74-III spherulites was achieved, while Maltese cross extinction pattern of spherulites was maintained, as indicated by the optical images, polarized optical images, and PXRD patterns (Figures 5D and S8). The mesoporosity in these series of spherulite superstructures provides new behaviors and rooms for guest recognition and transportation, which are extremely difficult to achieve in the traditional spherulite superstructures.

In addition to immobilizing soluble species, other MOF seeds can be utilized to construct hierarchical MOF spherulites by non-epitaxial growth. Guided by a retrosynthetic design, chemically stable Zr-based PCN-222(Fe) crystals were chosen as core





#### Figure 5. Introducing Multiple Components into MOF-74 Spherulites

(A) SEM and the corresponding EDX mapping of MOF-74-III(Zn/Co/Ni) spherulites.

(B) One-pot immobilization of multiple metal ions including  $Zn^{2+}$ ,  $Co^{2+}$ , and  $Ni^{2+}$  into MOF-74-III spherulites, the corresponding optical images, and polarized optical images.

(C) One-pot immobilization of functional species CoPc into MOF-74-III spherulites, the corresponding optical images, and polarized optical images. (D) Post-synthetic encapsulation of an organic dye (methylene blue) into MOF-74-III spherulites, the corresponding optical images, and polarized optical images.

(E) One-pot immobilization of PCN-222 into MOF-74-II spherulites, the corresponding optical images, and polarized optical images.

(F) PCN-222(Fe)@MOF-74-II catalyzed epoxidation of alkenes.

Scale bar, 25  $\mu m$  in (A) and 100  $\mu m$  in (B)–(E).

MOFs, which allow for the coating of MOF-74-II spherulites outside PCN-222(Fe).<sup>15</sup> The resulting PCN-222(Fe)@MOF-74-II spherulites contain distinct cores, which are different from previously described MOF-74 spherulites having undetected cores with innumerable fibers radiating from an apparent point nucleus, as indicated by optical and SEM images (Figures 5E, S15, and S16). The hierarchical PCN-222(Fe)@MOF-74-II superstructures can function as an efficient size-selective catalyst for olefin epoxidation reaction, because Fe-porphyrin moieties in the core PCN-222(Fe) can act as catalytic centers while the shell MOF-74-II spherulites with a limited channel size can control the substrate selectivity (Figures 5F and S18). It should be noted that the orientation of MOF-74 channels, radiating from the spherulite center, ensures the substrate transportation to the catalytically active PCN-222(Fe). We further studied the catalytic performance of PCN-222(Fe)@MOF-74-II during the epoxidation reaction involving olefins with different steric hindrance. As indicated by Table S1, small olefins including cyclopentene and cyclohexene showed efficient conversion due to the high accessibility of PCN-222(Fe) cores. When it came to larger olefins such as 1,2-diphenylethene and (E)-1-nitro-4-styrylbenzene, the conversion after 24 h was very limited, comparing with the PCN-222(Fe) without spherulite coating (Table S1). These results indicated the spherulite superstructures assembled from 1D fibers could limit the diffusion of large substrates, therefore providing a beneficial size-selective effect of hierarchical superstructures for catalysis.

#### DISCUSSION

In summary, we present an initial example of porous crystalline spherulite superstructures with well-arranged MOF crystallites. By controlling over nucleation and growth rates via a mixed-solvent approach, the kinetics of superstructure evolution can be well controlled, leading to the formation of various superstructures including spherulites and needle aggregates. The Maltese cross extinction pattern typical of spherulites under a polarized light was well-maintained during the isoreticular expansion and multicomponent introduction. Taking advantage of this hierarchical spherulite superstructures, we are able to control the encapsulation of guest molecules into the porous channels. Accordingly, our discovery here can be used not only to create porous MOF superstructures with tunable pore sizes but also to incorporate functional units within the hierarchical spaces of these superstructures, thereby offering a fresh route to the design and packing of three-dimensional sophisticated composites for applications in storage, delivery, and catalysis.

#### **EXPERIMENTAL PROCEDURES**

#### Synthesis of MOF-74-II Spherulite

 $Zn(NO_3)_2 \cdot 6H_2O$  (40 mg), Linker II (15 mg), EtOH (0.1 mL), H<sub>2</sub>O (0.1 mL), and DMF (2 mL) were charged into a Pyrex vial. The mixture was heated in 100°C oven for 24 h. After cooling down to room temperature, the colorless MOF-74-II spherulites were harvested.

#### Synthesis of MOF-74-III Spherulite

 $Zn(NO_3)_2 \cdot 6H_2O$  (40 mg), Linker III (15 mg), EtOH (0.1 mL), H<sub>2</sub>O (0.1 mL), and DMF (2 mL) were charged into a Pyrex vial. The mixture was heated in 100°C oven for 24 h. After cooling down to room temperature, the colorless MOF-74-III spherulites were harvested.

#### Synthesis of MOF-74-IV Spherulite

 $Zn(NO_3)_2 \cdot 6H_2O$  (40 mg), Linker IV (15 mg), EtOH (0.1 mL), H<sub>2</sub>O (0.1 mL), and DMF (2 mL) were charged into a Pyrex vial. The mixture was heated in 100°C oven for

24 h. After cooling down to room temperature, the colorless MOF-74-IV spherulites were harvested.

#### Experimental Procedure for Monitoring the MOF-74-III Spherulite Formation

 $Zn(NO_3)_2 \cdot 6H_2O$  (40 mg), Linker III (15 mg), EtOH (0.1 mL), H<sub>2</sub>O (0.1 mL), and DMF (2 mL) were charged into a Pyrex vial. The mixture was heated in 100°C oven for X h (X = 3, 4.5, 6, 8, and 24 h).

### Experimental Setup for the Influence of DEF on the MOF-74-III Spherulite Formation

 $Zn(NO_3)_2 \cdot 6H_2O$  (40 mg), Linker III (15 mg), EtOH (0.1 mL), H<sub>2</sub>O (0.1 mL), DMF (0, 0.5, 1.0, 1.5, and 2.0 mL, respectively) and DEF (2.0, 1.5, 1.0, 0.5, and 0 mL, respectively) were charged into a Pyrex vial. The mixture was heated in 100°C oven for 24 h.

#### SUPPLEMENTAL INFORMATION

Supplemental Information can be found online at https://doi.org/10.1016/j.chempr. 2019.12.001.

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#### **AUTHOR CONTRIBUTIONS**

Conceptualization, L.F. and H.-C.Z.; Methodology, L.F.; Investigation, L.F., K.-Y.W., and T.-H.Y.; Writing – Original Draft, L.F.; Writing – Review and Editing, K.-Y.W. and H.-C.Z.; Funding Acquisition, H.-C.Z.; Resources, H.-C.Z.; and Supervision, H.-C.Z.

#### **DECLARATION OF INTERESTS**

The authors declare no competing interests.

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