Supplemental information

Determining factors in the growth of MOF single crystals unveiled by *in situ* interface imaging

Jinli Han, Xudong He, Jin Liu, Ruijian Ming, Mohan Lin, Hui Li, Xiaochun Zhou, and Hexiang Deng
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Section S1. Supplemental experimental procedures

1.1 Chemicals

Copper (II) nitrate trihydrate (Cu(NO$_3$)$_2$·3H$_2$O), Cobalt chloride hexahydrate (CoCl$_2$·6H$_2$O), 2,5-Dihydroxyterephthalic Acid (DHTP), Terephthalic acid (BDC), Naphthalene-1,4-dicarboxylic acid (NDC), Benzimidazole (BIm), Trimesic acid (BTC), N,N-dimethylformamide (DMF), ethanol (EtOH), methanol (MeOH) were all purchased from China National Medicines Corporation LTD. All the materials were graded analytical at least and were used without any further purification.
1.2 Growth solution of Cu-MOF-74

![Diagram of Cu-MOF-74 and DHTP molecules]

**Figure S1.** The components of Cu-MOF-74 and the corresponding crystal structure.

**A. Solvothermal synthesis of Cu-MOF-74**

In this study, the Cu-MOF-74 crystals were synthesized using the similar procedure as reported with modifications for improving crystal crystallization rate. Specifically, 96.6 mg (0.40 mmol) of Cu(NO$_3$)$_2$·3H$_2$O in 2 mL MeOH were ultrasonically dissolved in a 20 mL vial. Then, 15.9 mg (0.08 mmol) of organic linkers DHTP in 2 mL mixed solvent (DMF and MeOH with volumetric ratio of 1:1) were ultrasonically dissolved in a 20 mL vial. The mixture of above solution was heated in a 65°C oven for 2 h. Brown rod-shaped crystals were formed after cooling down to room temperature.

**B. Cu-MOF-74 growth solution for in situ observation**

96.6 mg (0.40 mmol) of Cu(NO$_3$)$_2$·3H$_2$O in 2 mL MeOH were ultrasonically dissolved in a 20 mL vial. 15.9 mg (0.08 mmol) of organic linkers DHTP in 2 mL of mixed solvent (DMF and MeOH with volumetric ratio of 1:1) were ultrasonically dissolved in a 20 mL vial. The mixture of above solution was filtered by using the 220 nm syringe filter. After that, the growth solution was placed in an ice water bath to avoid crystals nucleation and growth.

The detailed growth conditions of Cu-MOF-74 for kinetic study are listed in Table S1, where the metal salts were dissolved in MeOH, and the organic linkers were dissolved in the mixed solvent (DMF and MeOH with volumetric ratio of 1:1). Each independent experiment included five growth conditions varying sequentially. Experiment #1, #2 and #3 corresponded to varying the concentrations of Cu$^{2+}$, varying the concentrations of organic linkers and varying the growth temperatures, respectively.
Table S1. The detailed growth conditions of Cu-MOF-74 for kinetic study.

<table>
<thead>
<tr>
<th>Experiments #</th>
<th></th>
<th>[Cu(NO₃)₂·3H₂O]</th>
<th></th>
<th>[DHTP]</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>V (mL)</td>
<td>[C] (mol·L⁻¹)</td>
<td>V (mL)</td>
<td>[C] (mol·L⁻¹)</td>
</tr>
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<td>2</td>
<td>0.04</td>
</tr>
<tr>
<td>B</td>
<td>1</td>
<td>2</td>
<td>0.08</td>
<td>2</td>
<td>0.04</td>
</tr>
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<tr>
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<tr>
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<td>2</td>
<td>0.10</td>
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<tr>
<td>I</td>
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</tr>
<tr>
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<td>0.20</td>
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<td>0.04</td>
</tr>
<tr>
<td>III</td>
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<td>0.04</td>
</tr>
<tr>
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<td>0.20</td>
<td>2</td>
<td>0.04</td>
</tr>
<tr>
<td>V</td>
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<td>0.20</td>
<td>2</td>
<td>0.04</td>
</tr>
</tbody>
</table>
1.3 Growth solution of Cu-MOF-2-BDC

![Diagram of growth solution]

**Figure S2.** The components of Cu-MOF-2-BDC and the corresponding crystal structure.

**A. Solvothermal synthesis of Cu-MOF-2-BDC**

The Cu-MOF-2-BDC crystals were synthesized using the similar procedure as reported with modifications for improving crystal crystallization rate.\(^2\) 108.7 mg (0.45 mmol) of Cu(NO\(_3\))\(_2\)-3H\(_2\)O were ultrasonically dissolved in 3 mL mixed solvent (DMF, EtOH and MeOH with volumetric ratio of 1:1:1) in a 20 mL vial. Then, 74.8 mg (0.45 mmol) of organic linkers BDC were ultrasonically dissolved in 3 mL DMF in a 20 mL vial. The mixture of above solution was heated in a 55°C oven for 2 h. Blue square plated-shaped crystals were formed after cooling down to room temperature.

**B. Cu-MOF-2-BDC growth solution for in situ observation**

108.7 mg (0.45 mmol) of Cu(NO\(_3\))\(_2\)-3H\(_2\)O were ultrasonically dissolved in 3 mL mixed solvent (DMF, EtOH and MeOH with volumetric ratio of 1:1:1) in a 20 mL vial. 74.8 mg (0.45 mmol) of organic linkers BDC in 3 mL of DMF were ultrasonically dissolved in a 20 mL vial. The mixture of above solution was filtered by using the 220 nm syringe filter. After that, the growth solution was placed in an ice water bath to avoid crystals nucleation and growth.

The detailed growth conditions of Cu-MOF-2-BDC for kinetic study are listed in Table S2, where the metal salts were dissolved in mixed solvent (DMF, EtOH and MeOH with volumetric ratio of 1:1:1), and the organic linkers were dissolved in DMF. Each independent experiment included five or six growth conditions varying sequentially. Experiment #1, #2 and #3 corresponded to varying the concentrations of Cu\(^{2+}\), varying the concentrations of organic linkers and varying the growth temperatures, respectively.
Table S2. The detailed growth conditions of Cu-MOF-2-BDC for kinetic study.

<table>
<thead>
<tr>
<th>Experiments</th>
<th>#</th>
<th>[Cu(NO₃)₂·3H₂O] V (mL)</th>
<th>[C] (mol·L⁻¹)</th>
<th>[BDC] V (mL)</th>
<th>[C] (mol·L⁻¹)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>A</td>
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<td>0.05</td>
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<td>0.15</td>
<td>55</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>3</td>
<td>0.10</td>
<td>3</td>
<td>0.15</td>
<td>55</td>
</tr>
<tr>
<td></td>
<td>C</td>
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<td>0.15</td>
<td>3</td>
<td>0.15</td>
<td>55</td>
</tr>
<tr>
<td></td>
<td>D</td>
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<td>3</td>
<td>0.15</td>
<td>55</td>
</tr>
<tr>
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<td>0.15</td>
<td>55</td>
</tr>
<tr>
<td>2</td>
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<td>3</td>
<td>0.05</td>
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</tr>
<tr>
<td></td>
<td>b</td>
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<td>0.10</td>
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</tr>
<tr>
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<td>3</td>
<td>0.15</td>
<td>55</td>
</tr>
<tr>
<td></td>
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<td>0.15</td>
<td>3</td>
<td>0.20</td>
<td>55</td>
</tr>
<tr>
<td></td>
<td>e</td>
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<td>0.15</td>
<td>3</td>
<td>0.25</td>
<td>55</td>
</tr>
<tr>
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<tr>
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<td>III</td>
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<tr>
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<td>61.3</td>
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</table>
1.4 Growth solution of Cu-MOF-2-NDC

![Diagram of Cu-MOF-2-NDC growth solution](image)

**Figure S3.** The components of Cu-MOF-2-NDC and the corresponding crystal structure.

**A. Solvothermal synthesis of Cu-MOF-2-NDC**

The Cu-MOF-2-NDC crystals were synthesized using the similar procedure as reported with modifications for improving crystal crystallization rate. 36.2 mg (0.15 mmol) of Cu(NO$_3$)$_2$·3H$_2$O in 3 mL mixed solvent (DMF, EtOH and MeOH with volumetric ratio of 1:1:1) were ultrasonically dissolved in a 20 mL vial. Then, 45.4 mg (0.21 mmol) of organic linkers NDC in 3 mL mixed solvent (DMF, EtOH and MeOH with volumetric ratio of 1:1:1) were ultrasonically dissolved in a 20 mL vial. The mixture was heated in a 55°C oven for 2 h. Green plate-shaped crystals were produced after cooling down to room temperature.

**B. Cu-MOF-2-NDC growth solution for in situ observation**

36.2 mg (0.15 mmol) of Cu(NO$_3$)$_2$·3H$_2$O in 3 mL mixed solvent (DMF, EtOH and MeOH with volumetric ratio of 1:1:1) were ultrasonically dissolved in a 20 mL vial. 45.4 mg (0.21 mmol) of organic linkers NDC in 3 mL mixed solvent (DMF, EtOH and MeOH with volumetric ratio of 1:1:1) were ultrasonically dissolved in a 20 mL vial. The mixture of above solution was filtered by using the 220 nm syringe filter. After that, the growth solution was placed in an ice water bath to avoid crystals nucleation and growth.

The detailed growth conditions of Cu-MOF-2-NDC for kinetic study are listed in Table S3, where the metal salts and organic linkers NDC were dissolved in mixed solvent (DMF, EtOH and MeOH with volumetric ratio of 1:1:1) except experiment #3. Each independent experiment included five growth conditions varying sequentially. Experiment #1, #2 and #3 corresponded to varying the concentrations
of Cu²⁺, varying the concentrations of organic linkers and varying the growth temperatures, respectively.

It was worth noting that, in order to compare the activation energies between Cu-MOF-2-BDC and Cu-MOF-2-NDC under the same solvent conditions, pure DMF rather than a mixed solvent (used in experiment #1 and #2) was used as the solvent for organic linkers in experiment #3.

Table S3. The detailed growth conditions of Cu-MOF-2-NDC for kinetic study.

<table>
<thead>
<tr>
<th>Experiments</th>
<th>#</th>
<th>[Cu(NO₃)₂·3H₂O]</th>
<th>[NDC]</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>V (mL)</td>
<td>[C] (mol·L⁻¹)</td>
<td>V (mL)</td>
<td>[C] (mol·L⁻¹)</td>
</tr>
<tr>
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<td>0.05</td>
<td>3</td>
<td>0.07</td>
</tr>
<tr>
<td>1</td>
<td>C</td>
<td>3</td>
<td>0.07</td>
<td>3</td>
</tr>
<tr>
<td>D</td>
<td>3</td>
<td>0.09</td>
<td>3</td>
<td>0.07</td>
</tr>
<tr>
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<td>3</td>
<td>0.03</td>
</tr>
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<td>2</td>
<td>c</td>
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<td>3</td>
</tr>
<tr>
<td>d</td>
<td>3</td>
<td>0.05</td>
<td>3</td>
<td>0.07</td>
</tr>
<tr>
<td>e</td>
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<td>0.05</td>
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<td>0.09</td>
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<tr>
<td>I</td>
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<td>V</td>
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<td>0.15</td>
</tr>
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</table>

C. Cu-MOF-2-NDC growth solution for the study of transition layer

The growth solutions of Cu-MOF-2-NDC for the study of transition layer were prepared, where the metal salts and organic linkers NDC were dissolved in mixed solvent (DMF, EtOH and MeOH with volumetric ratio of 1:1:1). Each growth solution was filtered by using the 220 nm syringe filter. Subsequently, the growth solution was placed in an ice water bath to avoid crystals nucleation and growth.

The experiment #1 was for intermittent growth at constant growth condition, where the constant growth solution and the solvent were alternately passed into the flow cell four times. The experiments #2 and #3 were for intermittent growth at different growth condition, where the growth solution with different concentration of Cu²⁺/organic linkers and the mixed solvent were alternately passed into the flow cell. The detailed growth conditions for the study of transition layer are listed in Table S4.
Table S4. The detailed growth conditions of Cu-MOF-2-NDC for transition layer study.

<table>
<thead>
<tr>
<th>Experiments</th>
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<th>[NDC]</th>
<th>Temperature ($^\circ$C)</th>
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<tbody>
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<td></td>
<td></td>
<td>V (mL)</td>
<td>[C] (mol·L$^{-1}$)</td>
<td>V (mL)</td>
</tr>
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<td></td>
<td></td>
</tr>
<tr>
<td>I</td>
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<td>0.15</td>
<td>3</td>
</tr>
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<td>II</td>
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<td>0</td>
<td>3</td>
</tr>
<tr>
<td>C</td>
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<td>D</td>
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<td>3</td>
</tr>
<tr>
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<td></td>
<td></td>
</tr>
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<td>3</td>
</tr>
<tr>
<td>b</td>
<td></td>
<td>3</td>
<td>0</td>
<td>3</td>
</tr>
<tr>
<td>c</td>
<td></td>
<td>3</td>
<td>0.15</td>
<td>3</td>
</tr>
<tr>
<td>d</td>
<td></td>
<td>3</td>
<td>0</td>
<td>3</td>
</tr>
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<tr>
<td>g</td>
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<tr>
<td>h</td>
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<td>3</td>
</tr>
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</table>
1.5 Synthesis and observation of Co-ZIF

**Figure S4.** The components of Co-ZIF and the corresponding crystal structure.

**A. Growth solution of Co-ZIF**

In this case, the Co-ZIF crystals were synthesized using the similar procedure as reported with modifications for improving crystal crystallization rate.\(^4\) 78.5 mg (0.33 mmol) of CoCl\(_2\)-6H\(_2\)O were ultrasonically dissolved in 3 mL MeOH in a 20 mL vial. Then, 198.5 mg (1.68 mmol) of organic linkers Blm were ultrasonically dissolved in 3 mL MeOH in a 20 mL Pyrex vial. The mixture was heated in a 50 °C oven for 2 h. Violet plate-shaped crystals were yielded after cooling down to room temperature.

**B. Co-ZIF growth solution for in situ observation**

78.5 mg (0.33 mmol) of CoCl\(_2\)-6H\(_2\)O were ultrasonically dissolved in 3 mL MeOH in a 20 mL vial. Then, 198.5 mg (1.68 mmol) of organic linkers Blm were also ultrasonically dissolved in 3 mL MeOH in a 20 mL vial. The mixture of above solution was filtered by using the 220 nm syringe filter. Subsequently, the growth solution was placed in an ice water bath to avoid crystals nucleation and growth.

The detailed growth conditions of Co-ZIF for kinetic study are listed in Table S5, where the metal salts and organic linkers Blm were dissolved in MeOH. Each independent experiment included four or five growth conditions varying sequentially. Experiment #1, #2 and #3 corresponded to varying the concentrations of Co\(^{2+}\), varying the concentrations of organic linkers and varying the growth temperatures, respectively.
Table S5. The detailed growth conditions of Co-ZIF for kinetic study.

<table>
<thead>
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<th>Experiments</th>
<th>#</th>
<th>[CoCl₂·6H₂O] V (mL)</th>
<th>[C] (mol·L⁻¹)</th>
<th>[BIm] V (mL)</th>
<th>[C] (mol·L⁻¹)</th>
<th>Temperature (°C)</th>
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<td>1</td>
<td>A</td>
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<td>B</td>
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<td>50</td>
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<tr>
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<td>C</td>
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<td>50</td>
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1.6 Growth solution of HKUST-1

**Figure S5.** The components of HKUST-1 and the corresponding crystal structure.

A. Solvothermal synthesis of HKUST-1

The HKUST-1 crystals were synthesized using the similar procedure as reported with modifications for improving crystal crystallization rate.\(^5\) 72.5 mg (0.30 mmol) of Cu(NO\(_3\))\(_2\)-3H\(_2\)O were ultrasonically dissolved in 3 mL mixed solvent (DMF, EtOH and H\(_2\)O with volumetric ratio of 1:1:1) in a 20 mL vial. Then, 12.6 mg (0.06 mmol) of organic linkers BTC were ultrasonically dissolved in 3 mL of DMF in a 20 mL vial. The mixture was heated in a 70 °C oven for 2 h. Blue octahedron-shaped crystals were yielded after cooling down to room temperature.

B. HKUST-1 growth solution for *in situ* observation

72.5 mg (0.30 mmol) of Cu(NO\(_3\))\(_2\)-3H\(_2\)O were ultrasonically dissolved in 3 mL mixed solvent (DMF, EtOH and H\(_2\)O with volumetric ratio of 1:1:1) in a 20 mL vial. Then, 12.6 mg (0.06 mmol) of organic linkers BTC were ultrasonically dissolved in 3 mL of DMF in a 20 mL vial. The mixture of above solution was filtered by using the 220 nm syringe filter. Subsequently, the growth solution was placed in an ice water bath to avoid crystals nucleation and growth.

The detailed growth conditions of HKUST-1 for kinetic study are listed in Table S6, where the metal salts were dissolved in mixed solvent (DMF, EtOH and H\(_2\)O with volumetric ratio of 1:1:1), and the organic linkers BTC were dissolved in DMF. Each independent experiment included five growth conditions varying sequentially. Experiment #1, #2 and #3 corresponded to varying the concentrations of Cu\(^{2+}\), varying the concentrations of organic linkers and varying the growth temperatures, respectively.
Table S6. The detailed growth conditions of HKUST-1 for kinetic study.

<table>
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<th>Experiments</th>
<th>#</th>
<th>[Cu(NO$_3$)$_2$·3H$_2$O]</th>
<th>[BTC]</th>
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Section S2. Morphology and structural characterizations

2.1 Illustration of MOF crystallization process

![Illustration of MOF crystallization process](image)

**Figure S6.** Three stages of MOF crystallization process including nucleation, crystal formation and evolution of crystal interface.

According to LAMER model, the crystallization process usually includes nucleation and growth. In this study, the crystallization process was divided into three parts based on the actual experimental conditions, including nucleation, formation of crystal and evolution of crystal interface (Figure S6). Here, we focus on the MOF crystal interface evolution stage after the formation of crystals in visible size, where small MOF crystals with defined shape and facets grow into larger size, to obtain kinetic information of MOF growth.
2.2 Illustration of DFM experimental setup

Figure S7. Illustration of DFM experimental setup and optical paths. (a) Experimental setup of DFM for *in situ* monitoring of MOF growth. (b) Optical paths of the light scattered at the interface of MOF single crystal.

As shown in Scheme 1A and Figure S7, the DFM experimental setup is composed of white light source, condenser lens, home-made flow cell, heating ring, objective lens and electron-multiplying CCD (EMCCD) camera from top to bottom. The white light is incident on the condenser lens, and then is converted into scattered light and irradiates on the MOF single crystals grown on the flow cell to give clear outlines of crystals.

There are three types of light paths irradiated on the single crystals, including scattered light, refracted light and reflected light. Only the scattered light at the edge of MOF crystal could be collected by the objective lens. While the refracted light could not pass through MOF crystals, and reflected light was kept away from the objective lens. Therefore, only four edges of each single MOF crystal were bright, while the mid part was always dark in DFM images, giving the clear outline of each MOF crystal. The entire interface evolution process of MOF crystals were collected and recorded by EMCCD camera.
2.3 Continuous flow cell setup

A. Introduction of continuous flow cell

![Continuous flow cell setup diagram]

**Figure S8.** Schematics of continuous flow cell setup. (a) Top view. (b) Bottom view.

The dimension of the flow cell is 76 mm×20 mm×0.32 mm as shown in Figure S8. There are two perfluoroalkoxy (PFA) tubes with inter diameter of 0.5 mm for feedstock inflowing and outflowing in the self-made flow cell. The PFA tube inlet of flow cell was connected to a vial containing pre-prepared stock solution, while the outlet of flow cell was connected to the micro injection pump for extracting stock solution into flow cell. The regular shaped cavity of flow cell was formed by sticking and encapsulating two pieces of glass plates in parallel, where the bottom glass was modified by gold nanoparticles as markers. Moreover, the electrical heating ring was placed beneath the flow cell to offer the energy for MOF growth.

B. The average fluid residence time (t) analysis

The volume of the flow cell chamber,

\[ V = 76 \times 20 \times 0.32 = 486.4 \text{ mm}^3 = 486.4 \mu\text{L} \quad \text{Eq. S1} \]

The flow rate was 2000 \( \mu\text{L}\cdot\text{min}^{-1} \) when the growth solution was exchanged by flushing in flow cell system, thus the average fluid residence time could be calculated,

\[ t = \frac{486.4 \mu\text{L}}{2000 \mu\text{L}\text{min}^{-1}} = 0.2432 \text{ min} = 14.6 \text{ s} \quad \text{Eq. S2} \]

In this study, the flow cell system was flushed for 30 sec when the growth solution was exchanged. This time is greater than average fluid residence time (14.6 s), thus the growth solution could be fully exchanged when the flow cell system was flushed.
C. Comparison of closed static reactor and continuous flow cell

![Comparison of closed static reactor and continuous flow cell](image)

**Figure S9.** Illustration for comparison between closed static reaction and continuous flowing reaction.

To systematically study the growth kinetics for MOF single crystals by *in situ* interface imaging method, it is desirable to provide stable concentration of metal ions and organic linkers at an appropriate flow rate during the period of MOF crystal growth. However, in a closed static reaction system that is typically employed in solvothermal synthesized MOF crystals, the concentrations gradually decrease over the time eventually MOF growth ceases as reactants are exhausted, where the concentration of growth solution cannot be determined in real time. Thus, these closed static reactors are not suitable to study the growth kinetics for MOF crystals. In response, a continuous flow cell was developed to enable MOF crystal growth under constant concentration (Figure S9). Specifically, flow cell offered an opportunity to control the crystal growth conditions, reduce the subtle difference of the individual crystal local chemical environment, and eliminate the diffusion effect of reactants, thus the concentration of metal salt and organic linkers could be kept constant throughout the crystal growth process. This allows for unveiling the separate influence from organic linkers, metal ions and reaction temperature. All growth kinetic studies of MOF crystals described here used this flow cell as reaction device.
2.4 DFM images of MOF growth process

The growth processes of multiple MOF crystals in the same field of view were monitored by \textit{in situ} time resolved DFM and recorded by EMCCD camera separately and collectively, giving up to 61200 frames DFM images. In order to clearly show the growth processes of these five types of MOF crystals, a series of DFM images were selected and shown here. The clear morphologies of these five typical MOFs with various dimensionalities were also offered by scanning electron microscope (SEM) images, which were taken in the same view of DFM image at the end of crystal growth. It was worth noting that the \textit{in situ} image recording was started at $t_0$, when there was sufficient amount of crystals reaching suitable size (1-2 μm) with their crystal interface visible. Therefore, some MOF crystals have appeared in the field of view of the microscope at $t_0$. This allowed us to focus on the evolution of crystal interface, avoiding influences from the initial nucleation process.
DFM images of Cu-MOF-74 growth process

**Figure S10.** Growth processes of multiple Cu-MOF-74 crystals monitored by *in situ* DFM. (a) A sequence of DFM images for the growth process of Cu-MOF-74 crystals at different times ($t_0 + 0$ s, $t_0 + 840$ s, $t_0 + 1200$ s, $t_0 + 1560$ s, $t_0 + 1920$ s, $t_0 + 2280$ s, $t_0 + 2640$ s, $t_0 + 3000$ s, $t_0 + 3360$ s, $t_0 + 3720$ s, $t_0 + 4080$ s, $t_0 + 4440$ s, $t_0 + 4800$ s, $t_0 + 5160$ s and $t_0 + 5520$ s) and SEM image corresponding to the same view of DFM images at the end of growth, the scale bar is 20 μm. (b) A sequence of DFM images for the growth process of one selected MOF single crystal, the scale bar is 5 μm. The images were cropped from another set of *in situ* experiment of Cu-MOF-74.
Figure S11. Growth processes of multiple Cu-MOF-2-BDC crystals monitored by in situ DFM. (a) DFM images of Cu-MOF-2-BDC crystals at initial time and final time, the scale bar is 20 μm. (b) SEM image corresponding to the same view of DFM images at the end of growth, the scale bar is 20 μm. (c) A sequence of DFM images for the growth process of Cu-MOF-2-BDC crystals at different times ($t_0 + 0$ s, $t_0 + 840$ s, $t_0 + 1080$ s, $t_0 + 1320$ s, $t_0 + 1560$ s, $t_0 + 1800$ s, $t_0 + 2040$ s and $t_0 + 2280$ s), the scale bar is 20 μm. The view area of DFM images was cropped from the white dashed box in (a). (d) A sequence of DFM images for the growth process of one selected MOF single crystal, the scale bar is 2 μm. The selected crystal was cropped and rotated from orange dashed box in (c).
DFM images of Cu-MOF-2-NDC growth process

**Figure S12.** Growth processes of multiple Cu-MOF-2-NDC crystals monitored by *in situ* DFM. (a) A sequence of DFM images for the growth process of Cu-MOF-2-NDC crystals at different times ($t_0 + 0$ s, $t_0 + 720$ s, $t_0 + 900$ s, $t_0 + 1080$ s, $t_0 + 1260$ s, $t_0 + 1440$ s, $t_0 + 1620$ s, $t_0 + 1800$ s, $t_0 + 1980$ s, $t_0 + 2160$ s, $t_0 + 2340$ s, $t_0 + 2520$ s, $t_0 + 2700$ s, $t_0 + 2880$ s and $t_0 + 3060$ s) and SEM image corresponding to the same view of DFM images at the end of growth, the scale bar is 20 μm. (b) A sequence of DFM images for the growth process of one selected MOF single crystal, the scale bar is 5 μm. The selected crystal was cropped and rotated from orange dashed box in (a).
DFM images of Co-ZIF growth process

Figure S13. Growth processes of multiple Co-ZIF crystals monitored by in situ DFM. (a) A sequence of DFM images for the growth process of Co-ZIF crystals at different times ($t_0 + 0\ s$, $t_0 + 120\ s$, $t_0 + 240\ s$, $t_0 + 360\ s$, $t_0 + 480\ s$, $t_0 + 600\ s$, $t_0 + 720\ s$, $t_0 + 840\ s$, $t_0 + 960\ s$, $t_0 + 1080\ s$, $t_0 + 1200\ s$, $t_0 + 1320\ s$, $t_0 + 1440\ s$, $t_0 + 1560\ s$ and $t_0 + 1680\ s$) and SEM image corresponding to the same view of DFM images at the end of growth, the scale bar is 20 μm. (b) A sequence of DFM images for the growth process of one selected MOF single crystal, the scale bar is 5 μm. The selected crystal was cropped and rotated from dashed box in (a).
Figure S14. Growth processes of multiple HKUST-1 crystals monitored by *in situ* DFM. (a) A sequence of DFM images for the growth process of HKUST-1 crystals at different times \((t_0 + 0 \text{ s}, t_0 + 360 \text{ s}, t_0 + 540 \text{ s}, t_0 + 720 \text{ s}, t_0 + 900 \text{ s}, t_0 + 1080 \text{ s}, t_0 + 1260 \text{ s}, t_0 + 1440 \text{ s}, t_0 + 1620 \text{ s}, t_0 + 1800 \text{ s}, t_0 + 1980 \text{ s}, t_0 + 2160 \text{ s}, t_0 + 2340 \text{ s}, t_0 + 2520 \text{ s} \text{ and } t_0 + 2700 \text{ s})\) and SEM image corresponding to the same view of DFM images at the end of growth, the scale bar is 20 μm. (b) A sequence of DFM images for the growth process of one selected MOF single crystal, the scale bar is 2 μm. The selected crystal was cropped and rotated from dashed box in (a).
2.5 SEM images

SEM images were used to examine the morphology of \textit{in situ} synthesized MOFs. After \textit{in situ} monitoring experiment, the flow cell was opened to get the bottom glass substrate, which was covered with \textit{in situ} synthesized MOF single crystals. This side of the glass substrate was sputtered with gold and then attached to the metal based sample holder. The same view of DFM observation field ought to be carefully looked for in SEM field. SEM measurements of \textit{in situ} synthesized MOFs were performed on the Quanta FEG 250 with accelerating voltage of 5 kV, 10 kV or 20 kV based on the electron beam stability of MOF crystals. Some other SEM images were recorded on the cold field emission SEM S-4800 with accelerating voltage of 5 kV. SEM measurements of solvothermal synthesized Cu-MOF-2-NDC were performed on the high resolution field-emission SEM (Verios 460) with accelerating voltage of 1 kV for size measurement.
Figure S15. SEM images of Cu-MOF-74 crystals in same view of DFM image. (a) DFM image of MOF crystals, the scale bar is 20 μm. (b) SEM image corresponding to the same view of DFM image in (a), the scale bar is 20 μm. (c) Enlarged view SEM images of some MOF crystals selected from (b), the scale bar is 5 μm. (d) DFM image of one selected Cu-MOF-74 single crystal, the scale bar is 5 μm. (e) SEM image corresponding to the same crystal in (d), the scale bar is 5 μm. (f) Partially enlarged view SEM images of the crystal in (e), the images in (d-f) were from another set of in situ experiment of Cu-MOF-74, the scale bar is 1 μm.
Figure S16. SEM images of Cu-MOF-2-BDC crystals in the same view of DFM image. (a) DFM image of multiple MOF crystals, the scale bar is 20 μm. (b) SEM image corresponding to the same view of DFM image in (a), the scale bar is 20 μm. (c) Enlarged view SEM images of some MOF crystals selected from (b), the scale bar is 2 μm.
Figure S17. SEM images of Cu-MOF-2-NDC crystals in the same view of DFM image. (a) DFM image of multiple MOF crystals, the scale bar is 20 μm. (b) SEM image corresponding to the same view of DFM image in (a), the scale bar is 20 μm. (c) Enlarged view SEM images of some MOF crystals selected from (b), the scale bar is 5 μm. (d) SEM image viewed from 45° corresponding to the same view of DFM image in (a), the scale bar is 20 μm. (e) Enlarged view SEM images viewed from 45° of some MOF crystals selected from (d), the scale bar is 5 μm.
Figure S18. SEM images of Co-ZIF crystals in the same view of DFM image. (a) DFM image of multiple MOF crystals, the scale bar is 20 μm. (b) SEM image corresponding to the same view of DFM image in (a), the scale bar is 20 μm. (c) Enlarged view SEM images of some MOF crystals selected from (b), the scale bar is 5 μm.
Figure S19. SEM images of HKUST-1 crystals in the same view of DFM image. (a) DFM image of multiple MOF crystals, the scale bar is 20 μm. (b) SEM image corresponding to the same view of DFM image in (a), the scale bar is 20 μm. (c) Enlarged view SEM images of some MOF crystals selected from (b), the scale bar is 2 μm.
2.6 Powder X-ray diffraction (PXRD)

PXRD was used to characterize the factivity and the phase purity of in situ synthesized MOFs in the flow cell. PXRD characterizations were performed on a Rigaku Smartlab 9 kW X-ray diffractometer operated at 45 kV, 200 mA for Cu Kα (λ = 1.5406 Å) with a scan speed of 5 °·min⁻¹ and a step size of 0.01° in 2θ at ambient temperature and pressure. Simulated MOFs PXRD patterns were calculated by the software “Materials studio 8.0” from the single crystal data.

Experimental PXRD patterns of solvothermal synthesized and in situ synthesized samples matched well with the patterns simulated from single crystal structures without any extra peaks, confirming the factivity and the phase purity of these in situ synthesized MOFs in the flow cell.

![Comparison of the in situ synthesized and solvothermal synthesized PXRD patterns of Cu-MOF-74 with the simulated Cu-MOF-74 diffraction pattern.](image)

**Figure S20.** Comparison of the in situ synthesized and solvothermal synthesized PXRD patterns of Cu-MOF-74 with the simulated Cu-MOF-74 diffraction pattern.
**Figure S21.** Comparison of the *in situ* synthesized and solvothermal synthesized PXRD patterns of Cu-MOF-2-BDC with the simulated Cu-MOF-2-BDC diffraction pattern.

**Figure S22.** Comparison of the *in situ* synthesized and solvothermal synthesized PXRD patterns of Cu-MOF-2-NDC with the simulated Cu-MOF-2-NDC diffraction pattern.
Figure S23. Comparison of the in situ synthesized and solvothermal synthesized PXRD patterns of Co-ZIF with the simulated Co-ZIF diffraction pattern.

Figure S24. Comparison of the in situ synthesized and solvothermal synthesized PXRD patterns of HKUST-1 with the simulated HKUST-1 diffraction pattern.
2.7 Crystal face indexing of Cu-MOF-2-NDC

In order to accurately determine the observed crystal facet of Cu-MOF-2-NDC single crystal with its crystal lattice, single crystal X-ray diffraction (SC-XRD) was used to index its crystal face. The crystal face index of Cu-MOF-2-NDC was measured on the Bruker AEX DUO using the Index Crystal Faces suite of APEX2 software. The data collection was carried out at ambient temperature and pressure.

Figure S25 showed that a single crystal was mounted on a glass fiber, and the unit cell was evaluated firstly to determine the orientation matrix. The index of all 6 faces of the plate-shaped crystal was (001), (010), (100), (001), (010), (100). According to the crystal edge of Cu-MOF-2-NDC indexed by SC-XRD, most of the square-shaped crystals observed in the flow cell were laying on the (001) facet and evolving along [010] and [100] directions to extend the edges of the square.

![Figure S25](image)

**Figure S25.** Crystal faces indexing results of Cu-MOF-2-NDC. (a) Square crystal face observed on DFM was assigned to {001} face. (b) Sides of square crystal face were assigned to {010} and {100} face. (c) Optical microscope image of {001} face. Insert is morphology of Cu-MOF-2-NDC. (d) Optical microscope image of {010} face. Insert is unit cell of Cu-MOF-2-NDC.
2.8 Atomic force microscope (AFM) images

AFM tapping mode was used for the further morphological and height analysis of Cu-MOF-2-NDC single crystals at room temperature. The measurements were performed on the Bruker Dimension ICON.

The comparison of DFM and AFM image of MOF single crystals in the same view indicated that the brightness of the crystal edges in DFM image was related to the thicknesses of the crystals. This is in good accordance to the increase in the height profile of MOFs in their *ex situ* AFM images taken at areas identical to the DFM images.

![Image](image.png)

**Figure S26.** Comparison of DFM image and AFM image of MOF single crystals in the same view and the height profiles of these three MOFs. (a) DFM image of three MOF crystals, the scale bar is 5 μm. (b) AFM image of these three MOF crystals in the same view of DFM image, the scale bar is 5 μm. (c) Corresponding height profiles of these three MOF crystals.
Section S3. Tracking MOF crystal interface evolution via super-resolution technique

3.1 Adopted procedure to obtain the growth curve of MOF single edge

The growth process of MOF crystals was in situ monitored by DFM platform and recorded as movies with a sequence of images. In order to accurately quantify the interface evolution process of MOF single crystal, super-resolution technique was applied to track the location of MOF interface at every moment. In this procedure, \( t_0 \) was chosen when there are sufficient amount of crystals reaching suitable size (1-2 \( \mu \text{m} \)) with their crystal interface visible. This allowed us to only focus on the evolution of crystal interface in the stage of crystal size extension, rather than at the nucleation stage at the very beginning, where the crystal interface is not distinguishable from the body in DFM images.

Here, we used a 2D square plate-shaped MOF, i.e. Cu-MOF-2-NDC as an example to introduce the super-resolution technique to track the location of MOF crystal edge. The size of Cu-MOF-2-NDC single crystal sounds small and the brightness of edges seems to be low at the earlier stage of growth in the bottom of Figure S27a, while the size of crystal seems large enough and the brightness of edges looks high at the later stage of recording on the top of the Figure S27a. As the crystal grew, the four bright edges of MOF single crystal extended outward gradually, but the center location of MOF single crystals remained stationary without obvious shift during the entire growth process. Based on the crystal face indexing results as shown in Figure S25, the crystal interface moved along \([010]\) and \([100]\) directions extending the edges of the square. Thus, taking the center of the crystal as the starting point (‘\( O \)’ in Figure S27a), the profile of light intensity along crystal growth direction could be obtained by super-line technique as shown in Figure S27b. With the growth of the single crystal, the position of peak in light intensity distribution curve moved outward continuously along with the gradually increasing of the light intensity. The shape of light intensity distribution curve was similar to Gaussian distribution along with the performance of the Gaussian fitting of the light intensity curve. Combining the previous discussion about scattered light on crystal edges and Gaussian distribution curve, the peak center of Gaussian distribution has been defined as \( X \), which was considered to be the location of the crystal edge, \( l \). The positions of peaks were labeled by red arrows in Figure S27b as an example. In the same way, the locations of other three edges of this selected MOF crystal could also be obtained.

Although the location of MOF single crystal edge in every frame could be determined by super-resolution technique. In order to improve quality of images, every 10 frames in recorded movie
were overlapped as one image to improve the trace resolution. Thus, growth curves of the selected MOF single crystal edges were obtained by combining every location of MOF edge at every moment. The four blue dashed lines as examples represented the locations of crystal edges at four moments ($t_0 + 300$ s, $t_0 + 700$ s, $t_0 + 1100$ s, and $t_0 + 1500$ s corresponding to Figure S27a) (Figure S27c).

**Figure S27.** Light intensity distribution curves of selected *in situ* synthesized Cu-MOF-2-NDC single crystal interfaces and growth curves of single crystal with respect to four sides. (a) Growth process of one selected Cu-MOF-2-NDC single crystal, the scale bar is 5 μm. (b) Gaussian fitting of light intensity distribution curves of MOF single crystal interfaces. (c) Growth curves of selected Cu-MOF-2-NDC single crystal edges.
3.2 Growth curves without and with markers referring

Figure S28. Growth curves without and with markers referring. (a) Some markers in DFM image, the scale bar is 20 μm. (b) The image-drift profile determined from averaged markers referring. (c, d) Growth curves of selected in situ synthesized Cu-MOF-2-NDC single crystal interfaces without (c) and with (d) markers referring.
3.3 Growth curves mergence for edges of MOF single crystal

Square-shaped MOF crystal, like Cu-MOF-2-NDC, owns four different growth curves obtained by super-line technique. In order to eliminate the influence of crystal nano-level movement, the growth curves of crystal interfaces ought to be merged to one growth curve representing the single crystal growth state. The details were described as the following.

**Figure S29.** Illustration of growth curve mergence principle. (a) Square crystal face. (b) Regular triangle crystal face.

The red point was defined as the ideal center point during crystal growth as shown in Figure S29. According to the feature of the square-shaped crystal, the distance $l$ between the center point and the edge is exactly the same. If the crystal did not shift during growth, the distance between the ideal center point and the edge was exactly the same at each moment, thus the growth curves of these four interfaces were identical. However, the crystals can not remain absolutely static during the actual growth process. In order to eliminate the influence of slight shift and represent the growth state of this crystal with one growth curve, the growth curves of these four interfaces ought to be merged.

Specifically, the black point was defined as the actual center point of the crystal at a certain moment during the crystal growth, which deviated from the ideal center position of the crystal. The actual distances between the black points and four crystal edges respectively were $l_1, l_2, l_3$ and $l_4$, where $l_1 \neq l_2 \neq l_3 \neq l_4$ in actual situation. However, according to the feature of the square-shaped crystal, the ideal distance $l$ between ideal center point and crystal edge could still be obtained by merged these actual distances based on the following mathematical equation.

$$ l = \frac{1}{4}(l_1 + l_2 + l_3 + l_4) \quad \text{Eq. S3} $$

The ideal distance $l$ between ideal center point and crystal edge at each moment could be obtained
in the same way. The growth curve of this crystal was obtained as shown in Figure S30b.

Similarly, the growth curves of regular triangle crystal face can be merged in the same way. In Figure S29b, $a$ represents the side length of the regular triangle, $h$ signifies the height of the regular triangle. The red point was defined as the ideal center point of the triangle crystal face at a certain moment. According to the feature of the regular triangle, the distance $l$ between the center point and three edges of the regular triangle ought to be exactly the same. If the crystal did not shift during the growth process, the ideal distance $l$ between the ideal center point and the three edges was exactly the same at each moment. The growth curves of these three edges obtained should be identical. However, the crystals can not remain absolutely static during the actual growth process. In order to eliminate the influence of slight shift and represent the growth state of this crystal with one growth curve, the growth curves of these three edges ought to be merged.

In the case of regular triangle, the relationship between ideal distance $l$ between the center to each edge of the regular triangle and the side length of regular triangle $a$ is given below,

$$l = \frac{\sqrt{3}}{6}a$$  \hspace{1cm} \text{Eq. S4}

And the relationship between the side length $a$ and height of regular triangle $h$ ought to be,

$$a = \frac{2\sqrt{3}}{3}h$$  \hspace{1cm} \text{Eq. S5}

Thus, the relationship between the distance $l$ and height of regular triangle $h$ is,

$$l = \frac{\sqrt{3}}{6}a = \frac{\sqrt{3}}{6} \times \frac{2\sqrt{3}}{3}h = \frac{h}{3}$$  \hspace{1cm} \text{Eq. S6}

The black point was defined as the actual center point of the crystal at a certain moment during the crystal growth, which deviated from the ideal center position of the crystal. The actual distances between the black points and three crystal edges respectively were $l_1$, $l_2$ and $l_3$, where $l_1 \neq l_2 \neq l_3$ in actual situation. According to the feature of the regular triangle, the sum of the distances from any point in the regular triangle to the three edges of the triangle ought to be equal to the height of regular triangle. The equation was described as the following.

$$h = l_1 + l_2 + l_3$$  \hspace{1cm} \text{Eq. S7}

The ideal distance $l$ between the ideal center point and the edge could still be obtained by merged these three distances based on the following mathematical equation.
The ideal distance $l$ between ideal center point and crystal edge at each moment could be obtained in the same way. Then the growth curve of this crystal was obtained as shown in Figure S30d.

**Figure S30.** The growth curves of different edges for MOF single crystal merged to one growth curve representing the growth state of crystal. (a, b) Before and after growth curves mergence for edges of square MOF single crystal. (c, d) Before and after growth curves mergence for edges of regular triangle MOF single crystal.
3.4 Growth curves of different MOFs with various dimensionalities

**Figure S31.** The growth curve of the selected *in situ* synthesized 1D Cu-MOF-74 single crystal edge.

(a) Growth process of one selected Cu-MOF-74 single crystal, the scale bar is 10 μm. (b) Growth curve of this Cu-MOF-74 single crystal edge with linear fitting.
Figure S32. The growth curves of the selected in situ synthesized 2D Cu-MOF-2-BDC single crystal. (a) Growth process of one selected Cu-MOF-2-BDC single crystal, the scale bar is 2 μm. (b) Growth curve of this Cu-MOF-2-BDC single crystal with linear fitting, the insert is growth curves of four edges for this single crystal.
**Figure S33.** The growth curves of the selected *in situ* synthesized 2D Co-ZIF single crystal. (a) Growth process of one selected Co-ZIF single crystal, the scale bar is 2 μm. (b) Growth curve of this Co-ZIF single crystal with linear fitting, the insert is growth curves of four edges for this single crystal.
Figure S34. The growth curves of the selected \textit{in situ} synthesized 3D HKUST-1 single crystal. (a) Growth process of one selected HKUST-1 single crystal, the scale bar is 2 μm. (b) Growth curve of this HKUST-1 single crystal with linear fitting, the insert is growth curves of three edges for this single crystal.
3.5 Trace resolution analysis of super-resolution technique used in this study

Trace resolution of super-resolution technique used in this study was carried out by selected a part of growth curve as shown in Figure S35b. Different from the general precision analysis, the growth curve with a time variable first ought to be converted to obtain residual of growth curve (Figure S35c). After that, the statistic histogram of the residual was collected and then fitted by Gaussian function to obtain the full width at half maximum (FWHM) value. The trace resolution of the super-resolution technique used in this study could reach 4.1 nm with the markers rectify based on FWHM value. It was worth noting that, the trace resolution may be not enough 4.1 nm at the initial stage of growth, due to the small size and low bright intensity of MOF crystal.

**Figure S35.** Trace resolution of super-resolution technique using in this study. (a) Growth curve of Cu-MOF-2-NDC crystal edge selected from Figure S30b. (b) A section of growth curve taken from (a). (c) Residual distribution around center of this section of growth curve. (d) Residual histograms corresponding to the curve in (c), where the FWHM value was 4.1 nm. Thus, the trace resolution of super-resolution technique used in this study could reach 4.1 nm with the markers rectify.
3.6 incident light would not offer energy for MOF growth

![Growth curve](image)

**Figure S36.** Growth curve of Cu-MOF-2-NDC at different growth temperature proved that incident light would not provide energy for MOF crystal growth.

The location of Cu-MOF-2-NDC single crystal edge extended from 2.25 μm to 3.30 μm at 50 °C, while the location of edge did not change after stopping heating, which indicated that crystal could not grow at room temperature due to the lack of energy. This demonstrated that incident light would not offer the energy for MOF growth.
Section S4. Mathematical model of growth rate for MOFs with various dimensionalities

The mathematic models of growth rate for MOF were developed to quantitatively study the growth rates of MOFs with various dimensionalities, including 1D rod-shaped, 2D plate-shaped and 3D octahedron-shaped MOFs, respectively. The details were described as the following.

4.1 Growth rate definition of 1D rod-shaped MOF

![Illustration of 1D rod-shaped MOF crystal growth rate definition.](image)

**Figure S37.** Illustrations of 1D rod-shaped MOF crystal growth rate definition.

As shown in Figure S37, where \( a \) is the length at the beginning of the rod-shaped crystal growth, \( b \) represents the diameter of the rod’s interface, \( S \) is the cross-sectional area of the rod-shaped crystal, and \( \Delta a \) and \( \Delta b \) are representing the change in lengths of crystal growth along the long axis and along the short axis during the period of time \( \Delta t \), respectively.

The reaction rate equation would be as follows,

\[
r = \frac{dc}{dt}
\]

Eq. S9

Where \( r \) is the growth rate of MOF crystal, and \( c \) is representing the local growth solution concentration of individual MOF crystal.

The relationship between the local growth solution concentration around individual MOF crystal \( c \) and MOF crystal mass \( m \) was described as the following,

\[
c = \frac{m}{MS}
\]

Eq. S10

Where \( m \) and \( M \) represent the mass and molar mass of MOF crystal, respectively.

Thus,

\[
dc = \frac{dm}{MS}
\]

Eq. S11

The relationship between crystal mass \( m \) and crystal volume \( V \) was described as the following,

\[
m = \rho V
\]

Eq. S12

Where \( \rho \) and \( V \) are the density and the volume of MOF crystal, respectively.

Growth rate \( r \) could be described by \( V \) and \( t \),
Then the volume of the crystal increased $\Delta V$ in the period of $\Delta t$. The growth rate could be described as the following,

$$
\frac{dV}{dt} = \frac{\Delta V}{\Delta t} = \frac{\pi}{4} \times \frac{(a + 2\Delta a)(b + 2\Delta b)^2 - ab^2}{\Delta t}
$$

Equation S14

$$
\approx \frac{\pi \times b^2 \Delta a}{2 \Delta t}
$$

$$
= \frac{\pi \times b^2}{2} \frac{da}{dt}
$$

Equation S15

Where $\Delta V$ is the increment of crystal growth volume during the period of time $\Delta t$.

Since the length along the short axis $\Delta b$ was too small and could be ignored, the content related to this item could be omitted (orange part in Eq. S14), thus the above equation could be organized as:

$$
\frac{dV}{dt} = \frac{\pi}{2} b^2 \frac{da}{dt}
$$

Equation S15

The cross-sectional area of the rod-shaped crystal $S$ could be obtained from the following equation,

$$
S = \frac{\pi}{4} b^2
$$

Equation S16

Based on above equations, the growth rate $r$ of rod-shaped crystal could be obtained,

$$
r = \frac{dc}{dt} = \frac{dm}{M \Delta t} = \frac{\rho dV}{M \Delta t} = \frac{\rho \pi b^2 \frac{da}{dt}}{M \frac{\pi}{4} b^2 \frac{da}{dt}} = \frac{2\rho \frac{da}{dt}}{M} \text{ slope}
$$

Equation S17

$$
= \frac{2\rho}{M} \text{ slope}
$$

Equation S18

Since the density and molar mass of the same MOF system are constant, the growth rate could be obtained as long as the slope of the growth curve obtained through linear fitting. The growth rate ‘$r$’ here was represented by slope of the linear fitting for growth curve in order to simplicity.
4.2 Growth rate definition of 2D plate-shaped MOFs

Figure S38. Illustrations of 2D plate-shaped MOF crystal growth rate definition.

As shown in Figure S38, where $a$ and $h$ were describing the side length and height at the beginning of the square plate-shaped crystal growth, $S$ is the cross-sectional area of the square plate-shaped crystal. $\Delta a$ and $\Delta h$ are representing the change in horizontal direction and vertical direction during the period of time $\Delta t$, respectively.

Based on reaction rate equation,

$$r = \frac{dc}{dt}$$  \hspace{1cm} \text{Eq. S9}

Where $r$ is the growth rate of MOF crystal, and $c$ is representing the local growth solution concentration of individual MOF crystal.

The relationship between the local growth solution concentration around individual MOF crystal $c$ and MOF crystal mass $m$ was described as the following,

$$c = \frac{m}{MS}$$  \hspace{1cm} \text{Eq. S10}

Where $m$ and $M$ represent the mass and molar mass of MOF crystal, respectively.

Thus,

$$dc = \frac{dm}{MS}$$  \hspace{1cm} \text{Eq. S11}

The relationship between crystal mass $m$ and crystal volume $V$ was described as the following,

$$m = \rho V$$  \hspace{1cm} \text{Eq. S12}

Where $\rho$ is the density of MOF crystal, and $V$ represents volume of MOF crystal.

Growth rate $r$ could be described by $V$ and $t$,

$$r = \frac{dc}{dt} = \frac{dm}{MSdt} = \frac{\rho dV}{MSdt}$$  \hspace{1cm} \text{Eq. S13}

Then the volume of the crystal increased $\Delta V$ in the period of $\Delta t$. Thus, the growth rate could be described as the following,
\[
\frac{dV}{dt} = \frac{\Delta V}{\Delta t} = \frac{(a + 2\Delta a)^2 \times (h + 2\Delta h) - a^2h}{\Delta t}
\]
\[
= \frac{[a^2 + 4a \times \Delta a + 4(\Delta a)^2] \times (h + 2\Delta h) - a^2h}{\Delta t}
\]
\[
= \frac{[a^2h + 2a^2 \times \Delta h + 4a \times \Delta a \times h + 8a \times \Delta a \times \Delta h + 4(\Delta a)^2 \times h + 8(\Delta a)^2 \times \Delta h] - a^2h}{\Delta t}
\]
\[
= \frac{4ah \times \Delta a}{\Delta t} = 4ah \times \frac{da}{dt}
\]

Where \(\Delta V\) is the increment of crystal growth volume during the period of time \(\Delta t\).

Since the length along the height \(\Delta h\) and product of \(\Delta a\) were too small and could be ignored, the content related to these items can be omitted (orange part and blue part in Eq. S19), and the above equation could be organized as:

\[
\frac{dV}{dt} = 4ah \frac{da}{dt}
\]  
Eq. S20

The cross-sectional area of the square plate-shaped crystal \(S\) could be obtained from the following equation,

\[
S = ah
\]  
Eq. S21

Based on above equations, the growth rate \(r\) of square plate-shaped crystal could be obtained,

\[
r = \frac{dc}{dt} = \frac{dm}{M \frac{dt}{dM}} = \frac{\rho dV}{M \frac{dt}{dM}} = \frac{\rho \times 4ahda}{Mahdt} = \frac{\rho da}{Mdt}
\]  
Eq. S22

\[
\rho' = 4\rho
\]  
Eq. S23

\[
\frac{da}{dt} \text{ was the slope of the linear fitting for growth curve. Thus,}
\]

\[
r = \frac{\rho'}{M} \cdot \text{slope}
\]  
Eq. S24

Since the density and molar mass of the same MOF system are constant, the growth rate could be obtained as long as the slope of the growth curve obtained through linear fitting. The growth rate ‘\(r\)’ here was represented by slope of the linear fitting for growth curve in order to simplicity.
4.3 Growth rate definition of 3D regular octahedron MOFs

**Figure S39.** Illustrations of 3D regular octahedron-shaped MOF crystal growth rate definition.

As shown in Figure S39, where \( a \) is the side length at the beginning of the 3D regular octahedron crystal growth, \( l \) is the vertical distance from the center point to the side, \( S' \) is the cross-sectional area of the octahedron crystal, \( S \) is the area of the triangle crystal face in DFM image, and \( \Delta l \) is the change in length of crystal growth along the direction perpendicular to the triangle side during the period of time \( \Delta t \).

Based on reaction rate equation,

\[
    r = \frac{dc}{dt} \quad \text{Eq. S9}
\]

Where \( r \) is growth rate of MOF crystal, and \( c \) is representing the local growth solution concentration of individual MOF crystal.

The relationship between the local growth solution concentration around individual MOF crystal \( c \) and MOF crystal mass \( m \) was described as the following,

\[
    c = \frac{m}{MS'} \quad \text{Eq. S10}
\]

Where \( m \) and \( M \) represent the mass and molar mass of MOF crystal, respectively.

Thus,

\[
    dc = \frac{dm}{MS'} \quad \text{Eq. S11}
\]

The relationship between crystal mass \( m \) and crystal volume \( V \) was described as the following,

\[
    m = \rho V \quad \text{Eq. S12}
\]

Where \( \rho \) is the density of MOF crystal, and \( V \) represents volume of MOF crystal.

Growth rate \( r \) could be described by \( V \) and \( t \),
It was worth noting that the growth curve of 3D regular octahedron-shaped MOF crystals obtained from our *in situ* DFM platform was based on the location of crystal edge, which was the distances \( l \) from the center points to the crystal edges, not the side lengths \( a \). The relationship between \( l \) and \( a \) was described as the following,

\[
l = \frac{\sqrt{3}}{6} a \quad \text{Eq. S26}
\]

Thus,

\[
V = \frac{\sqrt{2}}{3} a^3 = 8\sqrt{6}l^3 \quad \text{Eq. S27}
\]

Then the volume of the crystal increased \( \Delta V \) in the period of \( \Delta t \). Thus, the growth rate could be described as the following,

\[
\frac{dV}{dt} = \frac{\Delta V}{\Delta t} = 8\sqrt{6} \times \frac{(l + \Delta l)^3 - l^3}{\Delta t}
\]

\[
= 8\sqrt{6} \times \frac{[l^3 + 3l^2 \times \Delta l + 3l \times (\Delta l)^2 + (\Delta l)^3] - l^3}{\Delta t}
\]

\[
= 24\sqrt{6}l^2 \times \frac{\Delta l}{\Delta t}
\]

\[
= 24\sqrt{6}l^2 \times \frac{dl}{dt}
\]

Where \( \Delta V \) is the increment of crystal growth volume during the period of time \( \Delta t \).

Since \((\Delta l)^3\) and \((\Delta l)^3\) were too small and can be ignored, the content related to these items could be omitted (orange parts in Eq. S28), and the above equation could be organized as,

\[
\frac{dV}{dt} = 24\sqrt{6}l^2 \frac{dl}{dt} \quad \text{Eq. S29}
\]

The cross section of the regular octahedral crystal had an angle with the adjacent triangles, and there was a positive correlation between \( S \) and \( S' \). Thus a coefficient \( k \) could be introduced to express their relationship. The cross-sectional area of the regular octahedron-shaped crystal \( S' \) could be obtained from the following equation,

\[
S' = kS = 3\sqrt{3}kl^2 \quad \text{Eq. S30}
\]

Based on above equations, the growth rate \( r \) of the regular octahedron-shaped could be obtained,
\[
\frac{dc}{dt} = \frac{dm}{MS' dt} = \frac{\rho dV}{MS' dt} = \frac{24\sqrt{6}\rho l^2 dl}{M 3\sqrt{3}k l^3 dt} = \frac{8\sqrt{2}\rho dl}{M k dt}
\]

Eq. S31

\[
\rho' = \frac{8\sqrt{2}\rho}{k}
\]

Eq. S32

\[
\frac{dl}{dt}
\]

was the slope of the linear fit of the growth curve.

\[
r = \frac{\rho'}{M} \cdot \text{slope}
\]

Eq. S33

Since the density and molar mass of the same MOF system are constant, the growth rate could be obtained as long as the slope of the growth curve was obtained through linear fitting. The growth rate ‘\(r\)’ here was represented by slope of the linear fitting for growth curve in order to simplicity.

It was worth noting that crystals of isotropic shape are used here as the mathematic model to derive growth rate for MOFs. The actual crystal growth rate ‘\(r_a\)’ should be added a coefficient ‘\(\varphi\)’ to correct deviation caused by the difference in morphology and structure feature between different individual MOF single crystals.

\[
r_a = \varphi \cdot r
\]

Eq. S34

In fact, the actual value of crystal growth rate has little effect on the accuracy of the reaction order and activation energy, after taking logarithm on growth rate of crystal (Section S5 and S6). Therefore, the growth rate ‘\(r\)’ here was represented by slope of the linear fitting for growth curve in order to simplicity.

In addition, most crystals were observed in regular shapes in the SEM images (Figure S15-Figure S19), further demonstrating the rationality of this simplification.
Based on growth curves and growth rate definition of different MOFs (Cu-MOF-74, Cu-MOF-2-BDC, Cu-MOF-2-NDC, HKUST-1 and Co-ZIF), the growth rates of these MOFs can be obtained by linear fitting.

**Figure S40.** The growth curves of five typical MOFs with various dimensionalities and their corresponding growth rates. (a) Cu-MOF-74. (b) Cu-MOF-2-BDC. (c) Cu-MOF-2-NDC. (d) HKUST-1. (e) Co-ZIF.
Figure S41. The growth rate and structure feature of the individual MOF revealed by comparing DFM images and SEM images of the same region. (a, b) Initial and final DFM images of Cu-MOF-2-NDC single crystals, the scale bar is 20 μm. (c) SEM image corresponding to the same view of final DFM image with the growth rate of each individual MOF crystal labeled, the scale bar is 20 μm. (d, e) SEM images of representative MOF crystals, with no nearby crystals (d) and with crystal close by (e), the scale bar is 5 μm. (f, g) Growth curves of each individual MOF crystal in d. (h) Growth curves of crystals in e.

After scrutinizing the SEM image and the growth rate of the corresponding crystal in the DFM image, we found that the growth rate of single crystal might be sensitive to the adjacent crystal when they are too close (Figure S41e). The growth rate is usually lower than the average growth rate ($1.520 \pm 0.121$ nm·s$^{-1}$), for example 1.295, 1.345, 1.415 and 1.289 nm·s$^{-1}$, for crystal 2, 5, 9 and 10, respectively. Although the design of flow cell provide a relatively stable concentration around each single crystal to
give a linear growth behavior for majority of crystals (Figure S41f and g), there still might be competition between the adjacent crystal when their distance is close, reflected in the growth curves (Figure S41h). Such subtle difference is hardly observed in space averaged characterization methods, further demonstrating the power of this in situ interface imaging method.
5.1 Mathematical model of apparent reaction order and reaction rate constant

In order to further study the determining factor for the growth of MOF single crystal, such as concentrations of reactants and reaction temperature, it’s necessary to derive a mathematical model to establish the relationship between growth conditions and growth rate. The details were described as the following.

First, the determining factor of reactant concentration can be assessed by apparent reaction order, thus a mathematical model of reaction order for MOF growth was proposed. From the knowledge of physical chemistry, in the rate equation of a chemical reaction, the algebraic sum of the exponents of each substance concentration term are considered as the reaction order, usually represented by $n$. According to the feature of MOF growth, we used the isolation method to determine the apparent reaction order for metal ions and organic linkers, respectively.

Then mathematic model was built to describe the relationship between the growth rate ($r$) and the reaction order ($n$).

There is a simple chemical reaction as the following,

$$A(l) + B(l) + C(s) \xrightarrow{k} C(s)$$

Eq. S35

Where $A$ and $B$ represented the metal ions and organic linkers for MOF synthesis, respectively. $C_0$ and $C$ represented the crystal interface and the growth units of MOF, respectively.

At time $t$, the concentration of $A$ was $c_A$, the concentration of $B$ was $c_B$, and the reaction kinetic equation could be described as the following,

$$r = -\frac{dc}{dt} = k c_A^n c_B$$

Eq. S36

Where $k$ was reaction rate constant, and then taking logarithms on both sides of above equation,

$$\lg r = \lg(-\frac{dc}{dt}) = \lg k + m \lg c_A + n \lg c_B$$

Eq. S37

If the concentration of reactant $A$ and temperature was fixed and the concentration of reactant $B$ was varied sequentially, the term $m \lg c_A$ would be constant, which could be integrated with $\lg k$ to form $\lg k'$.

After simplification, the rate equation could be described as the following,
\[
\log r = \log k + m \log c_A + n \log c_B = \log k' + n \log c_B \quad \text{Eq. S38}
\]

Finally, the slope ‘n’ of above equation was the reaction order for reactant B. Based on this mathematic model, combining each synthetic concentration of reactant B and corresponded to growth rate, the reaction order of reactant B could be obtained by the linear fitting.

Moreover, the intercept is \(\log k'\), the reaction rate constant \(k\) could be obtained from intercept,

\[
\log k = \log k' - m \log c_A 
\quad \text{Eq. S39}
\]

In the same way, the reaction order for reactant A could also be obtained from the experiment varying the concentration of reactant A sequentially, while the concentration of reactant B and temperature are fixed.

Through the mathematical model of the reaction order and reaction rate constant for MOF growth, the apparent reaction orders and reaction rate constant for metal ions and organic linkers could be obtain respectively.

In order to further confirm the actual value of crystal growth rate ‘\(r_a\)’ has little effect on the accuracy of the reaction order, taking logarithm on growth rate of crystal. The details were described as the following.

The reaction order ‘m’ can be determined by linear fitting a series of \(\log r\) and \(\log c_A\) values to obtain the slope, which is the same after correcting the deviation using the actual crystal growth rate ‘\(r_a\)’.

\[
r_a = \varphi \cdot r 
\quad \text{Eq. S34}
\]

\[
\log(\varphi \cdot r) = \log k + m \log c_A + n \log c_B 
\quad \text{Eq. S40}
\]

\[
\log \varphi + \log r = \log k + m \log c_A + n \log c_B 
\quad \text{Eq. S41}
\]

\[
\log r = \log k + m \log c_A + n \log c_B - \log \varphi 
\quad \text{Eq. S42}
\]
5.2 Details to obtain apparent reaction order and rate constant of different MOFs

Here, we used the 2D square plate-shaped MOF, i.e. Cu-MOF-2-NDC as an example to introduce the methods to obtain the apparent reaction order for metal ions or organic linkers and rate constant. Firstly, the apparent reaction order for Cu$^{2+}$ was studied by fixing the concentration of organic linkers and reaction temperature (0.035 M, 50 °C). The concentrations of Cu$^{2+}$ were varied sequentially from low to high (0.015, 0.025, 0.035, 0.045 and 0.055 M). The growth curve of selected MOF single crystal was obtained as shown in Figure S46a, where the growth curve was divided into five segments and each segment corresponded to a synthetic concentration of Cu$^{2+}$. There were slight jitters in the growth curve when exchanging the growth solution of different concentrations, due to the flow cell flushed with the new feedstock for 30 s prior to recording. These slight jitters had little influence on the results of the growth rates, due to the flat region of each growth curve was used for linear fitting to obtain growth rate. The entire growth curve of this crystal was not a straight line, but the growth curve of each concentration stage was linear, which indicated that the crystal growth rate was constant under the same concentration, while the crystal growth rates were different at different synthetic concentrations. In order to quantitatively analyze the growth rate of this crystal at different concentrations, the growth curve of each concentration was linear fitted to give the growth rate at this concentration. The growth rates of this crystal at different concentrations were shown in Figure S46b, which showed clearly that the growth rate increased gradually with the synthetic concentration increasing. The growth rates were observed approximately linear with the concentrations of Cu$^{2+}$. Based on the mathematical model of apparent reaction order, after taking logarithms on both sides of reaction kinetic equation, the apparent reaction order of this selected MOF crystal for Cu$^{2+}$ was obtained as shown in Figure S46c. In the same way, the apparent reaction orders of other MOF crystals in the same view of DFM for Cu$^{2+}$ could also be obtained. Obviously, due to the influence of structure feature of different crystals and different local micro-chemical environment around MOF crystals, the apparent reaction orders of different crystals for Cu$^{2+}$ were also different.

In order to accurately determine the reaction order for Cu$^{2+}$, statistics analysis for all MOF crystals was performed. The statistical histogram of the apparent reaction orders for Cu$^{2+}$ was carried out as shown in Figure S46d. The accurate apparent reaction order of Cu-MOF-2-NDC for Cu$^{2+}$ and FWHM of this reaction order could be determined after Gaussian fitting, where the FWHM showed the
specificity of the crystal led by structure feature of different crystals and micro-chemical environment around the crystals rather than the errors.

Similarly, the reaction order for organic linkers could also be obtained by fixing the concentration of Cu$^{2+}$ and reaction temperature (0.025 M, 50 °C), the concentrations of organic linkers were varied sequentially (0.010, 0.015, 0.025, 0.035 and 0.045 M). The growth curve of this selected MOF single crystal was obtained as shown in Figure S48a. The growth rates at different concentrations and reaction order of this selected crystal were also obtained as shown in Figure S48b-c. Finally, the apparent reaction order of Cu-MOF-2-NDC for organic linkers was 0.49 by statistical analysis, and the FWHM of reaction order was 0.32 (Figure S48d).

In the same way, the apparent reaction orders for other typical MOFs with various dimensionalities were also assessed, including Cu-MOF-74, Cu-MOF-2-BDC, Co-ZIF, HKUST-1.
Figure S42. Apparent reaction orders of Cu-MOF-74 for Cu$^{2+}$. (a) Growth curve of the selected MOF single crystal, with various concentrations of Cu$^{2+}$ (0.02 mol·L$^{-1}$, 0.04 mol·L$^{-1}$, 0.06 mol·L$^{-1}$, 0.08 mol·L$^{-1}$ and 0.10 mol·L$^{-1}$). (b) Growth rates of the selected MOF single crystal at different Cu$^{2+}$ concentrations. (c) Apparent reaction order of this selected MOF single crystal for Cu$^{2+}$. (d) Statistics of apparent reaction order of Cu-MOF-74 for Cu$^{2+}$ collected based on multiple MOF single crystals.
Figure S43. Apparent reaction orders of Cu-MOF-74 for organic linkers, DHTP. (a) Growth curve of the selected MOF single crystal, with various concentrations of organic linkers (0.01 mol·L⁻¹, 0.02 mol·L⁻¹, 0.03 mol·L⁻¹, 0.04 mol·L⁻¹ and 0.05 mol·L⁻¹). (b) Growth rates of the selected MOF single crystal at different organic linker concentrations. (c) Apparent reaction order of this selected MOF single crystal for organic linkers. (d) Statistics of apparent reaction order of Cu-MOF-74 for organic linkers DHTP collected based on multiple MOF single crystals.
Figure S44. Apparent reaction orders of Cu-MOF-2-BDC for Cu$^{2+}$. (a) Growth curve of the selected MOF single crystal, with various concentrations of Cu$^{2+}$ (0.025 mol·L$^{-1}$, 0.050 mol·L$^{-1}$, 0.075 mol·L$^{-1}$, 0.100 mol·L$^{-1}$ and 0.125 mol·L$^{-1}$). (b) Growth rates of the selected MOF single crystal at different Cu$^{2+}$ concentrations. (c) Apparent reaction order of this selected MOF single crystal for Cu$^{2+}$. (d) Statistics of apparent reaction order of Cu-MOF-2-BDC for Cu$^{2+}$ collected based on multiple MOF single crystals.
Figure S45. Apparent reaction orders of Cu-MOF-2-BDC for organic linkers, BDC. (a) Growth curve of the selected MOF single crystal, with various concentrations of organic linkers (0.025 mol·L⁻¹, 0.050 mol·L⁻¹, 0.075 mol·L⁻¹, 0.100 mol·L⁻¹ and 0.125 mol·L⁻¹). (b) Growth rates of the selected MOF single crystal at different organic linkers concentrations. (c) Apparent reaction order of this selected MOF single crystal for organic linkers. (d) Statistics of apparent reaction order of Cu-MOF-2-BDC for organic linkers BDC collected based on multiple MOF single crystals.
Figure S46. Apparent reaction orders of Cu-MOF-2-NDC for Cu$^{2+}$. (a) Growth curve of the selected MOF single crystal, with various concentrations of Cu$^{2+}$ (0.015 mol·L$^{-1}$, 0.025 mol·L$^{-1}$, 0.035 mol·L$^{-1}$, 0.045 mol·L$^{-1}$ and 0.055 mol·L$^{-1}$). (b) Growth rates of the selected MOF single crystal at different Cu$^{2+}$ concentrations. (c) Apparent reaction order of this selected MOF single crystal for Cu$^{2+}$. (d) Statistics of apparent reaction order of Cu-MOF-2-NDC for Cu$^{2+}$ collected based on multiple MOF single crystals.

Figure S47. Apparent reaction orders of Cu-MOF-2-NDC for Cu$^{2+}$ with different batches. (a) Batch 1. (b) Batch 2.
**Figure S48.** Apparent reaction orders of Cu-MOF-2-NDC for organic linkers, NDC. (a) Growth curve of the selected MOF single crystal, with various concentrations of organic linkers (0.010 mol·L⁻¹, 0.015 mol·L⁻¹, 0.025 mol·L⁻¹, 0.035 mol·L⁻¹ and 0.045 mol·L⁻¹). (b) Growth rates of the selected MOF single crystal at different organic linkers concentrations. (c) Apparent reaction order of this selected MOF single crystal for organic linkers. (d) Statistics of apparent reaction order of Cu-MOF-2-NDC for organic linkers NDC collected based on multiple MOF single crystals.
Figure S49. Apparent reaction orders of Co-ZIF for Co$^{2+}$. (a) Growth curve of the selected MOF single crystal, with various concentrations of Co$^{2+}$ (0.035 mol·L$^{-1}$, 0.040 mol·L$^{-1}$, 0.045 mol·L$^{-1}$ and 0.050 mol·L$^{-1}$). (b) Growth rates of the selected MOF single crystal at different Co$^{2+}$ concentrations. (c) Apparent reaction order of this selected MOF single crystal for Co$^{2+}$. (d) Statistics of apparent reaction order of Co-ZIF for Co$^{2+}$ collected based on the edges of multiple MOF single crystals.
Figure S50. Apparent reaction orders of Co-ZIF for organic linkers, BIm. (a) Growth curve of the selected MOF single crystal, with various concentrations of organic linkers (0.32 mol·L⁻¹, 0.40 mol·L⁻¹, 0.48 mol·L⁻¹, and 0.56 mol·L⁻¹). (b) Growth rates of the selected MOF single crystal at different organic linkers concentrations. (c) Apparent reaction order of this selected MOF single crystal for organic linkers. (d) Statistics of apparent reaction order of Co-ZIF for organic linkers BIm collected based on the edges of multiple MOF single crystals.
Figure S51. Apparent reaction orders of HKUST-1 for Cu$^{2+}$. (a) Growth curve of the selected MOF single crystal, with various concentrations of Cu$^{2+}$ (0.01 mol·L$^{-1}$, 0.02 mol·L$^{-1}$, 0.03 mol·L$^{-1}$, 0.04 mol·L$^{-1}$ and 0.05 mol·L$^{-1}$). (b) Growth rates of the selected MOF single crystal at different Cu$^{2+}$ concentrations. (c) Apparent reaction order of this selected MOF single crystal for Cu$^{2+}$. (d) Statistics of apparent reaction order of HKUST-1 for Cu$^{2+}$ collected based on multiple MOF single crystals.
Figure S52. Apparent reaction orders of HKUST-1 for organic linkers, BTC. (a) Growth curve of the selected MOF single crystal, with various concentrations of organic linkers (0.01 mol·L⁻¹, 0.02 mol·L⁻¹, 0.03 mol·L⁻¹, 0.04 mol·L⁻¹ and 0.05 mol·L⁻¹). (b) Growth rates of the selected MOF single crystal at different organic linkers concentrations. (c) Apparent reaction order of this selected MOF single crystal for organic linkers. (d) Statistics of apparent reaction order of HKUST-1 for organic linkers BTC collected based on multiple MOF single crystals.
**Figure S53.** Apparent reaction orders of HKUST-1 for organic linkers, BTC with different batches. (a) Batch 1. (b) Batch 2. (c) Batch 3. (d) Batch 4.

**Figure S54.** Decrease in organic linkers concentration of HKUST-1 led to the promotion in the growth of MOF crystals. (a) Growth curve of the selected MOF single crystal, and the concentrations of organic linkers were 0.0025 mol·L⁻¹, 0.0020 mol·L⁻¹, 0.0015 mol·L⁻¹, 0.0010 mol·L⁻¹ and 0.0005 mol·L⁻¹, decreased gradually. (b) Growth rates of the selected MOF single crystal at different organic linkers concentrations.
Table S7. Summary of apparent reaction orders for metal and linker in the growth of different MOFs.

<table>
<thead>
<tr>
<th>MOFs</th>
<th>Chemical formulae</th>
<th>Gauss fitting</th>
<th>Statistics analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$m$ of metal ion</td>
<td>$n$ of organic linkers</td>
</tr>
<tr>
<td>Cu-MOF-74</td>
<td>$[\text{C}_6\text{H}_2\text{O}_2(\text{COO})_2]<em>n\text{Cu}</em>{2n}$</td>
<td>0.32</td>
<td>-0.12</td>
</tr>
<tr>
<td>Cu-MOF-2-BDC</td>
<td>$[\text{C}_6\text{H}_4(\text{COO})_2]_n\text{Cu}_n$</td>
<td>0.80</td>
<td>0.43</td>
</tr>
<tr>
<td>Cu-MOF-2-NDC</td>
<td>$[\text{C}_6\text{H}_2(\text{C}_4\text{H}_8)(\text{COO})_2]_n\text{Cu}_n$</td>
<td>1.09</td>
<td>0.49</td>
</tr>
<tr>
<td>Co-ZIF</td>
<td>$(\text{C}_7\text{H}_5\text{N}_2)_2\text{Co}_n$</td>
<td>2.92</td>
<td>2.12</td>
</tr>
<tr>
<td>HKUST-1</td>
<td>$[\text{C}_6\text{H}_3(\text{COO})_3]<em>2\text{Cu}</em>{3n}$</td>
<td>1.10</td>
<td>-1.14</td>
</tr>
</tbody>
</table>

The standard deviation of reaction order and activation energies was given to offer the statistical analysis (Table S7 and Table S9), in addition to the error bar based on the FWHM obtained from gauss fitting. It is worth mentioning that the peak location obtained by Gaussian fitting is in good agreement with the mean value obtained by statistical analysis, confirming the accuracy of our experimental results obtained from Gaussian fitting.
Rate constant is an important parameter for process assessment in chemical engineering, which directly reflects the reaction rate under a specific reaction condition. Rate constants of different MOF systems are given in Table S8. The growth rates calculated from rate constant are in good accordance to the experimental results (Figure S46b), confirming the accuracy of the reaction constant obtained.

Table S8. Summary of reaction rate constant ($k$) of different MOFs.

<table>
<thead>
<tr>
<th>MOFs</th>
<th>$k$ (nm/s/(mol/L)$^{m+n}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-MOF-74</td>
<td>6.99 ± 0.26</td>
</tr>
<tr>
<td>Cu-MOF-2-BDC</td>
<td>7.84 ± 0.35</td>
</tr>
<tr>
<td>Cu-MOF-2-NDC</td>
<td>163.30 ± 6.95</td>
</tr>
<tr>
<td>HKUST-1</td>
<td>0.13 ± 0.01</td>
</tr>
</tbody>
</table>
**Section S6. Activation energies of MOFs with various dimensionalities**

### 6.1 Mathematical model of activation energy

In order to further study the other critical aspect of MOF crystal growth kinetics, the activation energies were also assessed, the mathematical model of activation energy was based on the Arrhenius equation,

\[
\ln k = \ln A - \frac{E_a}{RT} \quad \text{Eq. S43}
\]

Where \( A \) and \( E_a \) are exponent factor and the activation energy, respectively, which are independent of the reaction conditions. \( k \) is reaction rate constant, \( T \) is reaction temperature and \( R \) is gas constant, \( 8.314 \, \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \). The logarithm of \( k \) is inversely proportional to the reaction temperature \( T \).

Thus, as long as the reaction rate constant \( k \) at different reaction temperature was measured, the activation energy \( E_a \) of this reaction can be determined based on Arrhenius equation. However, if the reaction rate constant \( k \) could not be obtained easily, the activation energy would also be obtained by only measuring the reaction rate. The detailed derivation process was as follows.

Taking an example of simple chemical reaction as the following

\[ A_{(l)} + B_{(l)} + C_{0(s)} \xrightarrow{k} C_{(s)} \quad \text{Eq. S35} \]

Where \( A, B \) and \( C_0 \) are the metal ions and organic linkers for the synthesis of MOFs, and crystal growth interface, respectively. \( C \) is representing the growth units of MOF.

At time \( t \), the concentration of \( A \) was \( c_A \), while the concentration of \( B \) was \( c_B \), the reaction kinetic equation can be described as the following,

\[
r = -\frac{dc}{dt} = kc_A^m c_B^n \quad \text{Eq. S36}
\]

Where \( k \) is reaction rate constant.

When activation energy of MOF was measured, the concentrations of the reactants \( (c_A, c_B) \) were fixed, and only the reaction temperature was varied sequentially. Since the temperatures had little influence on the reaction order based on physical chemistry knowledge. Thus, the reaction orders for metal ions and organic linkers \( (m, n) \) were remained constant. Then these terms including \( c_A, c_B \), \( m, n \) in above equation were all constants. The reaction rate constant can be described as the following,

\[
k = \frac{r}{c_A^m c_B^n} \quad \text{Eq. S44} \]
From this equation, the reaction rate $r$ was directly proportional to the reaction rate constant $k$. Then substituted this equation into the Arrhenius formula, that $k$ can be replaced with $r$ to obtain the relationship between reaction rate $r$ and reaction temperature $T$, described as the following,

$$\ln r = \ln A - \frac{E_a}{RT} + m \ln c_A + n \ln c_B$$  \hspace{1cm} \text{Eq. S45}

$$\ln r \propto 1/T$$  \hspace{1cm} \text{Eq. S46}

Finally, $-E_a/R$ can be determined by linear fitting a series of $\ln r$ and $1/T$ values to obtain the slope ‘$K$’.

Where,

$$K = -\frac{E_a}{R}$$  \hspace{1cm} \text{Eq. S47}

Thus,

$$E_a = -K \times R$$  \hspace{1cm} \text{Eq. S48}

In order to further confirm the actual value of crystal growth rate ‘$r_a$’ has little effect on the accuracy of the activation energy, taking logarithm on growth rate of crystal. The details were described as the following.

The activation energy ‘$E_a$’ will not change after correcting the deviation using the actual crystal growth rate ‘$r_a$’, due to taking logarithm on growth rate of crystal.

$$r_a = \varphi \cdot r$$  \hspace{1cm} \text{Eq. S34}

$$\ln(\varphi \cdot r) = \ln A - \frac{E_a}{RT} + m \ln c_A + n \ln c_B$$  \hspace{1cm} \text{Eq. S49}

$$\ln \varphi + \ln r = \ln A - \frac{E_a}{RT} + m \ln c_A + n \ln c_B$$  \hspace{1cm} \text{Eq. S50}

$$\ln r = \ln A - \frac{E_a}{RT} + m \ln c_A + n \ln c_B - \ln \varphi$$  \hspace{1cm} \text{Eq. S51}
6.2 Details to obtain activation energies of different MOFs

Here, we used the 2D square plate-shaped MOF, i.e. Cu-MOF-2-NDC as an example to introduce the methods to obtain the activation energy of MOF crystal. Firstly, the activation energy was explored by fixing the concentrations of metal ions and organic linkers (Cu2+: 0.075 M, organic linkers: 0.075 M) the reaction temperatures were varied sequentially from low to high (62.3 °C, 65.4 °C, 68.1 °C, 69.4 °C and 71.8 °C, respectively). The growth curve of selected MOF single crystal was obtained as shown in Figure S57a, where the growth curve was divided into five segments and each segment corresponded to a reaction temperature. The entire growth curve of this crystal is not a straight line, but the growth curve of each reaction temperature was linear, which indicated that the crystal growth rate was constant under the same reaction temperature while the crystal growth rates were different at different reaction temperature.

In order to quantitatively analyze the growth rate of the crystal at different reaction temperature, the growth curve of each reaction temperature was linearly fitted to give the growth rate at this reaction temperature. The growth rates of this crystal at different reaction temperatures were shown in Figure S57b, which showed clearly that the growth rate increased gradually with the reaction temperature increasing. The growth rates were approximately linear with the reaction temperatures.

Based on the Arrhenius formula and mathematical model of activation energy, the activation energy of this selected MOF crystal was obtained as shown in Figure S57c. In the same way, the activation energies of other MOF crystals in the same view of DFM could also be obtained. Obviously, the activation energies of different crystals were different due to the influence of structure feature of individual crystals and different local micro-chemical environment around the crystals.

In order to accurately determine the activation energy of Cu-MOF-2-NDC, statistics analysis for all MOF crystals was carried out. The statistical histogram of the activation energies of all crystals was Gaussian fitted. After that the accurate activation energy of Cu-MOF-2-NDC and FWHM of activation energy were determined as shown in Figure S57d.

Similarly, the activation energies of other typical MOFs with various dimensionalities were also assessed, including Cu-MOF-74, Cu-MOF-2-BDC, Co-ZIF, HKUST-1.
**Figure S55.** Activation energy of Cu-MOF-74. (a) Growth curve of the selected MOF single crystal at different temperatures, and the reaction temperatures were 58.0 °C, 60.2 °C, 62.3 °C, 64.4 °C and 67.2 °C increased gradually. (b) Growth rates of the selected MOF single crystal at different temperatures. (c) Activation energy analysis of this Cu-MOF-74 single crystal. (d) Activation energy of Cu-MOF-74 based on the statistical analysis of more than 50 crystals.
Figure S56. Activation energy of Cu-MOF-2-BDC. (a) Growth curve of the selected MOF single crystal at different temperatures, and the reaction temperatures were 49.7 °C, 52.0 °C, 54.4 °C, 57.4 °C, 59.0 °C and 61.3 °C increased gradually. (b) Growth rates of the selected MOF single crystal at different temperatures. (c) Activation energy analysis of this Cu-MOF-2-BDC single crystal. (d) Activation energy of Cu-MOF-2-BDC based on the statistical analysis of more than 50 crystals.
Figure S57. Activation energy of Cu-MOF-2-NDC. (a) Growth curve of the selected MOF single crystal at different temperatures, and the reaction temperatures were 62.3 °C, 65.4 °C, 68.1 °C, 69.4 °C and 71.8 °C increased gradually. (b) Growth rates of the selected MOF single crystal at different temperatures. (c) Activation energy analysis of this Cu-MOF-2-NDC single crystal. (d) Activation energy of Cu-MOF-2-NDC based on the statistical analysis of more than 50 crystals.
Figure S58. Activation energy of Co-ZIF. (a) Growth curve of the selected MOF single crystal at different temperatures, and the reaction temperatures were 44.8 °C, 45.8 °C, 47.0 °C, 48.6 °C and 50.1 °C increased gradually. (b) Growth rates of the selected MOF single crystal at different temperatures. (c) Activation energy analysis of this Co-ZIF single crystal. (d) Activation energy of Co-ZIF based on the statistical analysis of more than 30 crystals.
**Figure S59.** Activation energy of HKUST-1. (a) Growth curve of the selected MOF single crystal at different temperatures, and the reaction temperatures were 62.5 °C, 67.0 °C, 71.4 °C, 75.2 °C and 79.3 °C increased gradually. (b) Growth rates of the selected MOF single crystal at different temperatures. (c) Activation energy analysis of this HKUST-1 single crystal. (d) Activation energy of HKUST-1 based on the statistical analysis of more than 100 crystals.

**Table S9.** Summary of activation energies for five typical MOFs.

<table>
<thead>
<tr>
<th>MOFs</th>
<th>Gauss fitting</th>
<th>Statistics analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_a$ (kJ·mol$^{-1}$)</td>
<td>FWHM for $E_a$ (kJ·mol$^{-1}$)</td>
</tr>
<tr>
<td>Cu-MOF-74</td>
<td>115.6</td>
<td>20.2</td>
</tr>
<tr>
<td>Cu-MOF-2-BDC</td>
<td>59.9</td>
<td>23.7</td>
</tr>
<tr>
<td>Cu-MOF-2-NDC</td>
<td>82.1</td>
<td>19.6</td>
</tr>
<tr>
<td>Co-ZIF</td>
<td>73.6</td>
<td>45.4</td>
</tr>
<tr>
<td>HKUST-1</td>
<td>71.3</td>
<td>28.6</td>
</tr>
</tbody>
</table>
Figure S60. SEM images of Cu-MOF-2-NDC to count the crystal size and growth rate synthesized at different growth conditions. (a) SEM image of Cu-MOF-2-NDC synthesized at growth condition I. (b) SEM image of Cu-MOF-2-NDC synthesized at the same temperature and reaction time but growth condition II to increase the concentration of Cu\(^{2+}\). (c) SEM image of Cu-MOF-2-NDC synthesized at the same temperature and reaction time but growth condition III to increase the concentrations of both Cu\(^{2+}\) and organic linkers. (d) Growth rates of Cu-MOF-2-NDC at different growth conditions, and the corresponding theoretical value obtained through the apparent reaction orders.
**Table S10.** Summary of the fastest growth rate for different MOFs with solvothermal synthesis.

<table>
<thead>
<tr>
<th>Dimensionalities</th>
<th>MOFs</th>
<th>Growth rate (nm·s⁻¹)</th>
<th>References</th>
</tr>
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<tbody>
<tr>
<td>1D</td>
<td>Cu-MOF-74</td>
<td>10.2</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>CFA-17</td>
<td>4.2</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>Cu-s</td>
<td>1.75</td>
<td>8</td>
</tr>
<tr>
<td>2D</td>
<td>Cu-MOF-2-BDC</td>
<td>0.67</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>Cu-MOF-2-NDC</td>
<td>3.79</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>Co-ZIF</td>
<td>3.68</td>
<td>This work</td>
</tr>
<tr>
<td>3D</td>
<td>HKUST-1</td>
<td>2.38</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>HKUST-1</td>
<td>6.6</td>
<td>9</td>
</tr>
</tbody>
</table>
Figure S61. Growth curves of different crystal interfaces for Cu-MOF-2-NDC at constant concentration growth solution and bare solvent alternatively.

The rapidly falling process was found to exist simultaneously on the growth curves of the four crystal interfaces. This indicated that when the chemical environment around the crystal was replaced with bare solvent, the crystal interface dissociated quickly rather than the shift of crystal.
Figure S62. The growth curves of Cu-MOF-2-NDC single crystals with different chemical environment and flow rate. (a) Almost unaltered growth curve when the flow rate of the growth solution switched from 20 μL·min⁻¹ to 200 μL·min⁻¹. (b) The observation of crystal interface retreat when the growth solution was replaced by pure solvent at a constant flow rate of 20 μL·min⁻¹.

The further experiment was performed, where the reactant solutions were flowed at higher rates (200 μL·min⁻¹ as shown in Figure S62a). The crystal interfaces extend continuously as expected, rather than the growth interruption. This is completely different from the retreat of the transition layer (Figure S62b), confirming that the transition layer was not ‘washed off’ by the physical force, but the dissociation of building blocks from the transition layer.
Figure S63. Transition layer of Cu-MOF-2-NDC found from growth curve exchanging growth solution with constant concentration and bare solvent alternatively. (a) Growth curve of the selected MOF single crystal exchanging growth solution with constant concentration and bare solvent alternatively. (b) Growth rates of MOF crystals at different exchanging cycles. (c) Thickness of transition layers at different growth stage based on the averaging analysis of multiple crystals, \( l \) is distance between crystal interface at (001) facet and crystal center.
\[
\frac{dV}{dt} = \frac{\Delta V}{\Delta t} = \frac{(a + 2\Delta a)^2 \times (h + 2\Delta h) - a^2 h}{\Delta t}
\]

\[
= \frac{[a^2 + 4a \times \Delta a + 4(\Delta a)^2] \times (h + 2\Delta h) - a^2 h}{\Delta t}
\]

\[
= \frac{[a^3 h + 2a^2 \times \Delta h + 4a \times \Delta a \times h + 8a \times \Delta a \times \Delta h + 4(\Delta a)^2 \times h + 8(\Delta a)^2 \times \Delta h) - a^2 h}{\Delta t}
\]

\[
= \frac{4ah \times \Delta a}{\Delta t}
\]

\[
= 4ah \times \frac{da}{dt}
\]

Eq. S19

The morphology of the 2D MOF crystal, Cu-MOF-2-NDC, indicate that the extension length in the horizontal direction ($\Delta a$) is much greater than the extension length in the vertical direction ($\Delta h$), $\Delta a \gg \Delta h$ (Figure S38). Where $a$ and $h$ were the side length and height at the beginning of the square plate-shaped crystal growth. $\Delta a$ and $\Delta h$ represented the change in lengths of crystal growth along the side and along the height during the period of time $\Delta t$, respectively. Note that $\Delta h$ here describes the increase in the vertical height in the crystal growth process, different from the thickness of the soluble transition layer $\Delta H$ in Figure 4.

Based on above Eq. S19 and $\Delta a \gg \Delta h$, the contributions from $\Delta h$ and $(\Delta a)^2$ are relatively small, hence negligible. The result obtained from crystal volume or one-dimension sizes ($a$, $a = 2l$), is essentially same, and the overall crystal growth can be estimated from its horizontal interface extension. Therefore, the correlation is performed between the interface retreat thickness ($\Delta H$) and the one-dimension size of crystal rather than the crystal volume.
Figure S64. Transition layer of Cu-MOF-2-NDC found from growth curve exchanging growth solution with constant concentration and bare solvent alternatively in another experimental batch. (a) Growth curve of the selected MOF single crystal exchanging growth solution with constant concentration and bare solvent alternatively in another experimental batch. (b) Growth rate of MOF crystals at different exchanging cycles. (c) Thickness of transition layers at different growth stage based on the averaging analysis of multiple crystals.
Figure S65. Transition layer of Cu-MOF-2-NDC found from growth curve exchanging growth solution with different concentration of Cu$^{2+}$ and bare solvent alternatively. (a) Growth curve of the selected MOF single crystal exchanging growth solution with different concentration of Cu$^{2+}$ and bare solvent alternatively. (b) Growth rates of MOF crystals at different concentration of Cu$^{2+}$. (c) Thickness of transition layers at different growth stage based on the averaging analysis of multiple crystals, $l$ is distance between crystal interface at (001) facet and crystal center.
Figure S66. Transition layer of Cu-MOF-2-NDC found from growth curve exchanging growth solution with different concentration of organic linkers and bare solvent alternatively. (a) Growth curve of the selected MOF single crystal exchanging growth solution with different concentration of organic linkers and bare solvent alternatively. (b) Growth rate of MOF crystals at different concentration of organic linkers. (c) Thickness of transition layers at different growth stage based on the averaging analysis of multiple crystals, $l$ is distance between crystal interface at (001) facet and crystal center.
Figure S67. The relationship between thickness of transition layer concentration of growth solution and growth rate. (a) The relationship between height of transition layer and concentration of growth solution. (b) The relationship between height of transition layer and growth rate.
Figure S68. The relationship between thickness of transition layer and concentration of growth solution. The trends are different for different growth conditions. (a) Concentration of growth solution was constant. (b) Concentration of Cu$^{2+}$ was varied from low to high. (c) Concentration of organic linkers was varied from low to high. (d) Concentration of organic linkers was varied from high to low.
Figure S69. The relationship between growth rate and thickness of transition layer at different growth conditions. The trends are different for different growth conditions. (a) Concentration of growth solution was constant. (b) Concentration of Cu²⁺ was varied from low to high. (c) Concentration of organic linkers was varied from low to high. (d) Concentration of organic linkers was varied from high to low.
Figure S70. The relationship between thickness of transition layer and crystal size at different growth conditions. The trends are similar for different growth conditions. (a) Concentration of growth solution was constant. (b) Concentration of Cu$^{2+}$ was varied from low to high. (c) Concentration of organic linkers was varied from low to high. (d) Concentration of organic linkers was varied from high to low. $l$ is distance between crystal interface at (001) facet and crystal center.
The competition between accumulation and dissociation of molecular building blocks occurs on transition layer at MOF crystal interface. Energy might be a good angle to understand this interface retreat behavior. The difference between the transition layer and the crystalline core is reflected in their solubility in pure solvent. Although the transition layer can be dissolved, the crystalline core remains almost unaltered in the flow of pure solvent, which is not exactly the same as dissolution behavior of classic ionic solid as described by Madelung energy. The underlying reason, however, is similar, where the binding energy between the linker and metal containing building blocks in the crystalline core is much higher than that in the transition layer.
Section S8. Possible mechanisms of Cu-MOF-2

Consider a simple chemical reaction as follows,

\[ A(i) + B(i) + C_0(i) \xrightarrow{k} C(s) \] \hspace{1cm} Eq. S35

Where \( A, B \) and \( C_0 \) respectively represented the metal ions, organic linkers and crystal interface of MOF, respectively. \( C \) represented growth units of MOF.

Three possible mechanisms were proposed here (Figure 5), including,

Mechanism 1. Monomer-by-monomer addition mechanism

Mechanism 2. Mechanism involves the formation and direct accumulation of \( \text{Cu}_2\text{L}_4 \) SBU

Mechanism 3. Mechanism involves the formation of \( \text{Cu}_2\text{L}_4 \) SBU and its fragmentation into \( \text{CuL}_2 \)

The reaction orders derived from these three mechanisms were compared with the apparent reaction orders obtained from experiments.

The reaction orders of mechanism 1 and 2 were inconsistent with the experimental results. The reaction order of mechanism 3 matched well with the experimental results. The details for growth mechanism 3 of Cu-MOF-2 were proposed as the following.

Firstly, free organic linkers combined with \( \text{Cu}^{2+} \) to form the paddle wheel-type SBU (\( \text{Cu}_2\text{L}_4 \)) quickly, which was considered as a fast reaction process. Then the SBU divided into two smaller species (\( \text{CuL}_2 \)), and these smaller species combined with each other to form SBU reversibly, which was a fast equilibrium process followed by the reaction rate constants as \( k_1 \) and \( k_{-1} \), respectively. Based on the fast equilibrium approximation, the relationship between \( \text{CuL}_2 \) and \( \text{Cu}_2\text{L}_4 \) can be described as the following,

\[
K = \frac{k_1}{k_{-1}} = \frac{[\text{Cu}_2\text{L}_4]^2}{[\text{CuL}_2]^2} \] \hspace{1cm} Eq. S52

\[
[\text{Cu}_2\text{L}_4] = \sqrt{K[\text{CuL}_2]} \] \hspace{1cm} Eq. S53

\[
[\text{Cu}_2\text{L}_4] \approx \left(\frac{k_1}{k_{-1}}\right)^{\alpha_s}[\text{SBU}]^{\alpha_s} \] \hspace{1cm} Eq. S54

Finally, the \( \text{CuL}_2 \) combined with \( \text{Cu}^{2+} \) to form the MOF growth unit \( \text{Cu}_2\text{L}_2 \), which was a rate-determining step.
\[
\frac{d(CuL)}{dt} = k_1 [CuL][Cu^{2+}] = k_2 \left( \frac{k}{k_{\text{irr}}} \right)^{0.5} [Cu^{2+}][L]^{0.5}
\]

Eq. S55

The reaction orders of Cu\(^{2+}\) and organic linkers derived from this mechanism were 1.0 and 0.5 respectively, matched well with the experimental results of Cu-MOF-2.
9.1 The effect of molecular diffusion coefficients

Crystal growth is a dynamic process, involving the building blocks diffusing towards the interface, their consumption from and release to the solution, etc. In order to extract useful kinetic information in this process, a delicate balance is required, and this is one of the key challenges in this study.

The assessment of molecular diffusion coefficient here might be estimated from static reaction system, where the equation developed by Wilke and Chang,\(^\text{10}\) given below, can be used to predict liquid diffusivity.

\[
D_L = \frac{1.173 \times 10^{-13} (\phi M)^{0.5} T}{\mu V_m^{0.6}}
\]

where $D_L$ = liquid diffusivity, m\(^2\)/s,

$\phi$ = an association factor for the solvent,

$M$ = molecular mass of solvent,

$\mu$ = viscosity of solvent, mN s/m\(^2\),

$T$ = temperature, K,

$V_m$ = molar volume of the solute at its boiling point, m\(^3\)/kmol.

According to this equation, the difference in molecular diffusion coefficient in our systems studied only depends on the molar volume of the solute at its boiling point. Thus, the molecular diffusion coefficient of metal ions should be less than that of organic linker, due to the smaller molar volume of metal ions than that of organic linker. The metal ions indeed moved faster than the organic linkers to the surface of MOF crystal.

However, such difference in diffusion coefficient does not affect the crystal growth, when appropriate flow rate is applied, $\geq 10$ \(\mu\)L·min\(^{-1}\) (Figure 1E, Figure S62a and Figure S72b). This is because the flow of stock solution carries sufficient amount of metal and linker building blocks to the interface, where their diffusion is not a determining factor. The role of diffusion becomes critical, on the other hand, when the flow rate is relatively slow, where the demand of building block consumption at the interface is not met by the supply, e.g. at the flow rate of 2 \(\mu\)L·min\(^{-1}\) (Figure S72a). Therefore, a flow rate of 20 \(\mu\)L·min\(^{-1}\) is used here for the study of MOF growth, to give a growth curve that is almost linear at a fixed condition.
Figure S72. The growth curves of Cu-MOF-2-NDC single crystals at different flow rates. (a) 2 μL·min⁻¹, (b) 10 μL·min⁻¹.

The flow system is different from the stationary reaction that commonly used for MOF synthesis, in that the reactants (metal and linker) consumed in the crystal growth might be compensated in the flow system if an appropriate flow rate is applied. When a relatively slow flow rate is used, e.g. 2 μL·min⁻¹ of stock solution (Cu²⁺ and NDC with concentration of 0.15 and 0.10 mol·L⁻¹, respectively) for the growth of Cu-MOF-2-NDC, the consumption will be more than the supply, resulting in a gradually decreasing MOF crystal growth rate (Figure S72a). However, if the flow rate reaches 10 μL·min⁻¹ of the same stock solution with the other conditions identical, the growth rate is kept constant throughout the entire process of MOF crystal growth (Figure S72b).
Figure S73. Concentration distribution of the stock solution around single crystals. (a) Cu$^{2+}$. (b) Organic linker NDC.

Additional fluid flow simulations were also performed explain the effect of molecular diffusion coefficients. The concentration distribution of metal and linker, Cu$^{2+}$ and NDC for the growth of Cu-MOF-2-NDC crystals, is generally even around the crystals, at the concentration of 0.025 and 0.035 mol·L$^{-1}$, respectively (Figure S73). The simulation also reveals that a subtle decrease of concentration for NDC, on the level of $10^{-4}$ mol·L$^{-1}$, occurs between crystals that are too close in position (bottom right corner in Figure S73b). This provides reasonable explanation for the relatively smaller growth rate observed (Figure S41).
9.2 The effect of slip boundary conditions

Figure S74. Overlay of initial and final DFM images and center points of MOF crystals. (a) Overlay of initial and final DFM images of Cu-MOF-2-NDC with schematic diagram. (b) The positions of initial and final center points of Cu-MOF-2-NDC crystals.

The slip boundary conditions might exist, and further influence the growth of MOF on the inner surface of glass. If this were the case, the center of MOF crystal would have been moved during the growth process. Under the flow rate of 20 μL·min⁻¹, the majority of MOF single crystals remain stationary without obvious shift during the entire growth process, as supported by overlapping the initial and final DFM images of MOF crystal growth (Figure S74). Therefore, the slip boundary conditions, if exist, have little influence on MOF crystal growth in this study.
Figure S75. The flow rate distribution of the stock solution at different heights from the bottom in the flow cell, the field of view by the camera is marked with square.

The fluid flow simulations were further performed based on the dimensionality of the flow cell and the flow rate. It is clear that mass transfer process was not affected, where the flow rate of the stock solution is even at the same height, especially in the field of view marked by the square in the center (Figure S75). This matches well with the unaltered position of MOFs during their growth observed in the experiment. Such stability provides strong support for the quantitative analysis of the interface evolution.
9.3 The effect of shear stress of fluid

Figure S76. Assessment for the effects from fluid shear stress on the growth rate of MOF crystals. (a) Illustration of crystal growth direction and fluid direction in the flow cell, side A and B grow against the fluid, while side -A and -B grow along the fluid. (b) MOF crystals in the DFM image marked by the growth directions. (c) The growth rates at four different sides of five representative MOF crystals in the DFM image. (d) The statistics of growth rate at four different sides of all crystals in the DFM image, where the values are essentially the same.

In order to assess the influence from the shear stress, the growth rate of individual single crystal at different directions was monitored (Figure S76), where the side A and B grew against the fluid, while side -A and -B grew along the fluid. No obvious change was detected for the growth rate at different sides. Thus, under the experimental flow rate (20 \(\mu\)L·min\(^{-1}\)), the macroscopic crystal growth is not affected by the fluid shear stress, even if it exists.
Figure S77. The effects from fluid shear stress on the square-shaped Cu-MOF-2-NDC crystals. (a) The total deformation of MOF crystals affected by shear stress, the color of crystals is used to distinguish the crystals with or without shear stress. (b) The shear stress distribution of MOF crystals.

In addition, fluid flow simulations are performed, where the overall deformation for a crystal of 7 μm in size is $2.0 \times 10^{-11}$ nm, too small to be noticed (Figure S77a). The results also show that maximum shear stress occurs at the corners of square-shaped Cu-MOF-2-NDC crystal, but the value is on the level of $10^4$ Pa, negligible for the MOF growth (Figure S77b).
Table S11. Details of parameters for fluid flow simulations.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimension of flow cell</td>
<td>76 mm×20 mm×0.32 mm</td>
</tr>
<tr>
<td>Concentration of Cu(NO$_3$)$_2$</td>
<td>0.025 mol·L$^{-1}$</td>
</tr>
<tr>
<td>Concentration of NDC</td>
<td>0.035 mol·L$^{-1}$</td>
</tr>
<tr>
<td>Flow rate</td>
<td>20 μL·min$^{-1}$</td>
</tr>
<tr>
<td>Flow rate of outlet</td>
<td>1.7 m·s$^{-1}$</td>
</tr>
<tr>
<td>Density of mixed solution</td>
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<tr>
<td>Dynamic viscosity of mixed solution</td>
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</tr>
<tr>
<td>Growth rate of Cu-MOF-2-NDC</td>
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</tr>
<tr>
<td>Molecular diffusion coefficient of Cu(NO$_3$)$_2$ (assumption)</td>
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</tr>
<tr>
<td>Molecular diffusion coefficient of NDC (assumption)</td>
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<tr>
<td>Crystal density</td>
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<tr>
<td>Tensile yield strength</td>
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</tr>
<tr>
<td>Tensile ultimate strength</td>
<td>3.3E+07 Pa</td>
</tr>
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</table>
Supplemental references


