Supplementary Information for Manuscript entitled "Uniform and directional growth of centimeter-sized single crystals of cyclodextrin-based metal organic frameworks." by N. Kim, J. H. Park, and J. Paczesny*, and Bartosz A. Grzybowski*

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Section 1. Materials and synthetic methods

Materials for preparing CD-MOF single crystal

All reagents and solvents used were commercially available and, unless otherwise noted, were used as received without further purification.

Preparation of CD-MOF crystals: γ-cyclodextrin (> 99.0 %, from Tokyo Chemical Industry), rubidium hydroxide hydrate - $RbOH{\cdot}xH_2O$ (85%, Sigma Aldrich), cesium hydroxide monohydrate - $CsOH{\cdot}H_2O$ (≥99.5 % trace metals basis, Sigma Aldrich), and agarose (Bioreagent, for molecular biology, low EEO, Sigma Aldrich).

Preparation of stained AuNPs@CD-MOF: $HAuCl_4$ (≥ 99.9 %, Sigma Aldrich),

Preparation of PDMS mold for directional growth of CD-MOF single crystal: poly(dimethylsiloxane) (PDMS, Sylgard 184, Dow corning) and homemade aluminum stamps for shaping mold.

Synthetic method of CD-MOF2 (Rb) and CD-MOF (Cs) single crystal

Preparation of millimeter scale CD-MOF crystals: γ-cyclodextrin (1297 mg, 1 molar equivalent) and RbOH (820 mg, 8 molar equivalents) or CsOH (1343 mg, 8 molar equivalents;) were dissolved in 20 mL of deionized H_2O. The solution was filtered through a 0.45 μm PTFE membrane syringe filter and divided into five pre-washed vials (4 mL in each vial; vial diameter 2.7 cm , height 5.7 cm)at room temperature (~ 24 ºC). Each vial was capped with parafilm in which several (five to seven) needle-sized (~0.6 mm in diameter) holes were punctured. The parafilm was further covered with a 2.5-mm-thick layer of 2% w/w agarose gel whose role was to slow down diffusion of the outside solvent. The vial was then placed in a larger chamber (9 cm in diameter and 9.5 cm in height) filled with a mixture of methanol and H_2O (3:2 v/v for CD-MOF-2 (Rb) and 8:1 v/v for CD-MOF-3 (Cs); see discussion below for the role of MeOH:

H_2O ratio) which was allowed to vapor-diffuse into the growth solution over a period of up to 60 days. After that time, transparent crystals were obtained: up to 6-7 mm cubes for CD-MOF-2 (Rb) and 6-7 mm truncated cubooctahedra for CD-MOF-3 (Cs).

Preparation of centimeter scale CD-MOF crystals: Reseeding was done by placing a single crystal in a vial (diameter 2.7 cm , height 5.7 cm) filled with a saturated solution of γ-CD (1 mmol) and either (i) RbOH (8 mmol) in 6 mL of 5:1 v/v water/methanol mixture for CD-MOF-2 (Rb) or (ii) CsOH (8 mmol) in 8 mL of 5:3.5 v/v water/methanol mixture for CD-MOF-3 (Cs); these solutions were first filtered through a 0.45 μm PTFE membrane syringe filter. The vial was capped with punctured parafilm and agarose, and placed in a larger chamber (cf. above) filled with 49 mL of a 4:3 v/v mixture of MeOH and H_2O. The vapors of this mixture were allowed to vapor-diffuse into the saturated solution for two weeks.

N_2 gas sorption isotherms of CD-MOF crystals for BET surface area analysis

General information

Gas sorption isotherms were measured with ASAP 2020 volumetric adsorption equipment at 77 K. Typically, a sample of as-synthesized materials (~100 mg) was loaded.

Pore activation of CD- MOF crystals before gas adsorption experiments

The CD-MOF-2 (Rb) and CD-MOF-3 (Cs) single crystals were grinded. Crystals were soaked in methanol for 2 h and exchanged by fresh one. Solution was sonicated for 10 min and centrifuged at 7000 rpm for 20 min. This process was sequentially repeated 10 times. Then, washed samples were soaked in acetonitile and the washing process performed again with this solvent. The acetonitile-exchanged sample of each CD-MOF was evacuated at 50 ℃ for 2 days in ~10^{-3} mbar. Before adsorption measurement, additional activation at 90 ℃ for 3 hrs was performed to remove all gas or solvents in the sample.

Structural characterization of the CD-MOF single crystals or polycrystalline powders

Powder X-ray Diffraction (PXRD) spectra were collected on a Rigaku Miniplex 600 D/tex equipped with a Cu-sealed tube (λ=1.54178 Å). The following conditions were used: 40 kV, 15 mA, step: 0.01°, scan speed = 2 deg/min. Morphologies of water influence in CD-MOF crystallization were imaged by scanning electron microscopy (SEM, Hitach S-4800).

Section 2. Crystallinity of CD MOF-2(Rb) depending on reaction conditions

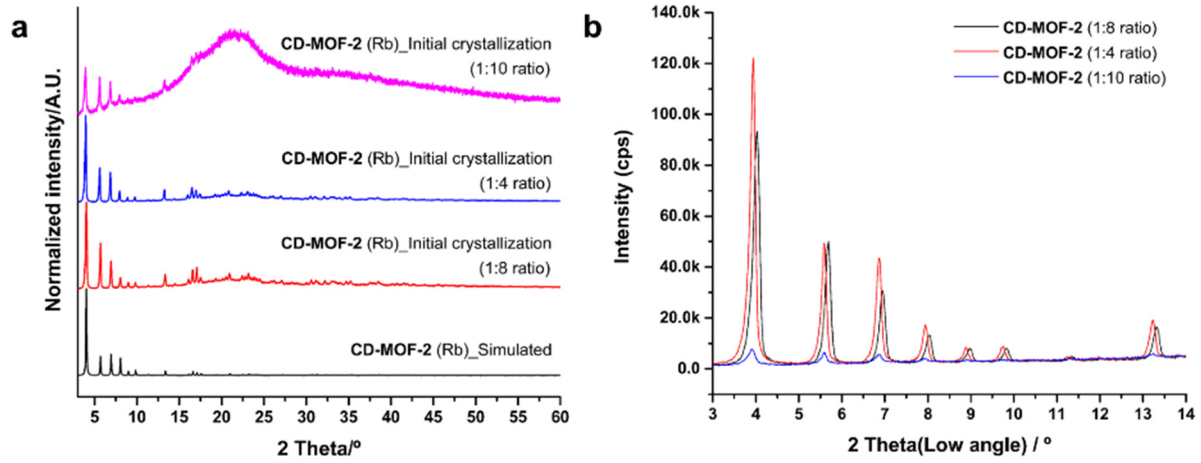


Fig. S1 (a) Powder X-ray Diffraction (PXRD) pattern of CD-MOF-2 (Rb) initial crystallization (Ligand to Metal ratio is 1:8, 1:4, and 1:10) and simulated pattern of CD-MOF-2 (Rb). **(b)** Absolute PXRD intensity for analyzing crystallinity of CD-MOF-2 (Rb) in each batch.

Section 3. Maintaining crystallinity after staining (AuNPs@CD-MOF)

Preparation of AuNPs@CD-MOF: The procedure was based on our previously published method for the preparation of core/shell, nanoparticle-doped architectures within MOF crystal.[S1]

In short, millimeter-sized CD-MOF crystals were soaked in 1.5 mM $HAuCl_4$ acetonitrile solution for 50 h. To remove the remaining salt, the as-prepared Au NP@CD-MOF crystals were washed with fresh acetonitrile 2 ~ 3 times over 24 h after the soaking process.

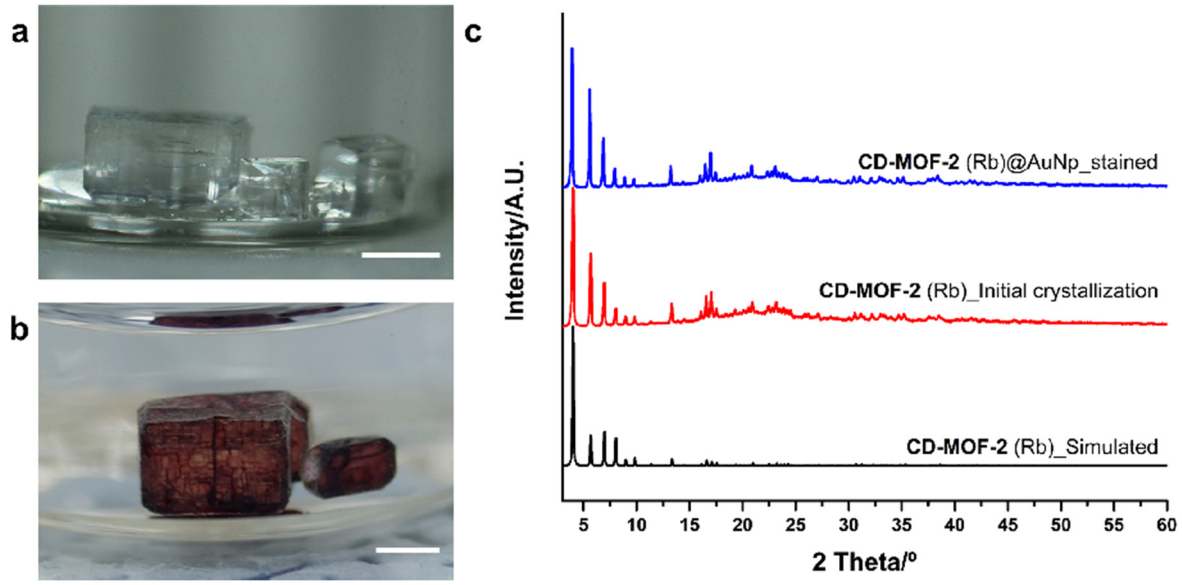


Fig. S2 Optical image of CD-MOF-2 (Rb) **(a)** before staining and **(b)** after staining. Scale bars correspond to 2 mm. **(c)** The PXRD pattern of before and after staining CD-MOF-2 (Rb) by Au NPs.

Section 4. Morphology of CD-MOF-2 (Rb) crystals depending on crystal growth conditions

Bulk mixing: γ-cyclodextrin (129.7 mg, 0.1 molar equivalent; from Tokyo Chemical Industry) and RbOH (82 mg, 0.8 molar equivalents; Sigma-Aldrich) were dissolved in 2 mL of deionized H_2O. The solution was filtered through a 0.45 μm PTFE membrane syringe filter and pull into pre-washed vial (2 mL in each vial; vial diameter 1.5 cm , height 4.5 cm) and mixed with 0.75 mL of pure methanol ($Crystal_{MeOH\ added}$) or mixture of 3:2 v/v water and methanol ($Crystal_{H_2O/MeOH\ added}$) at room temperature (~ 24 ºC). The mixture was sonicated for 15 min at 40 kHz. White powder was obtained inside the solution.

Layered diffusion method: γ-cyclodextrin (129.7 mg, 0.1 molar equivalent) and RbOH (82 mg, 0.8 molar equivalents) were dissolved in 2 mL of deionized H_2O. The solution was filtered through a 0.45 μm PTFE membrane syringe filter and pull into pre-washed vial (2 mL in each vial; vial diameter 1.5 cm , height 4.5 cm) and layered carefully with 0.75 mL of pure methanol ($Crystal_{MeOH\ added}$) or mixture of 3:2 v/v water and methanol ($Crystal_{H_2O/MeOH\ added}$) at room temperature (~ 24 ºC). White powder was obtained followed the layer between two solutions.

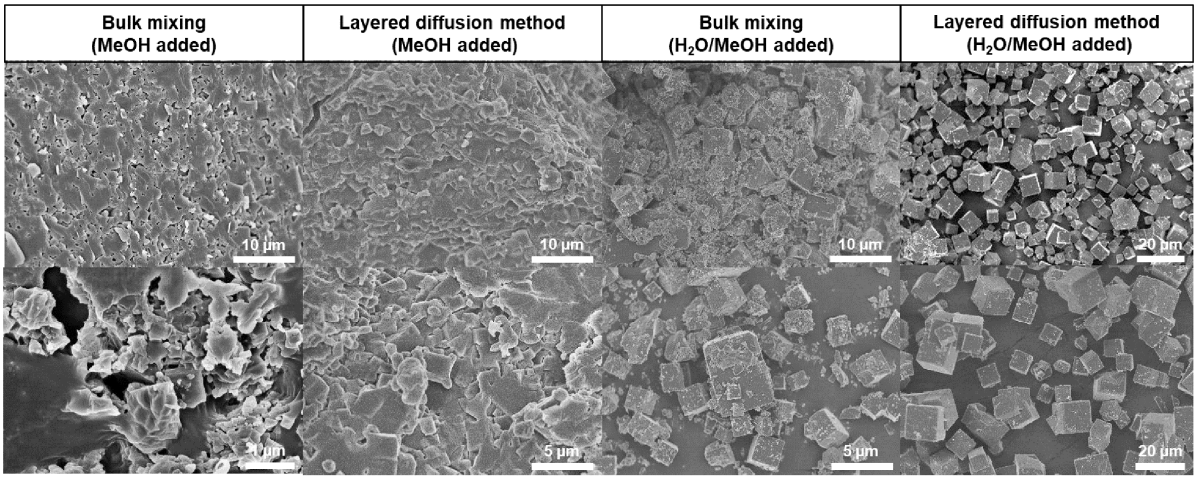


Fig. S3 SEM images of prepared CD-MOF-2 (Rb) crystals by bulk mixing and layered diffusion method.

Section 5. Additional optical images of centimeter-sized scale CD-MOF-2 (Rb) and CD-MOF-3 (Cs) single crystals

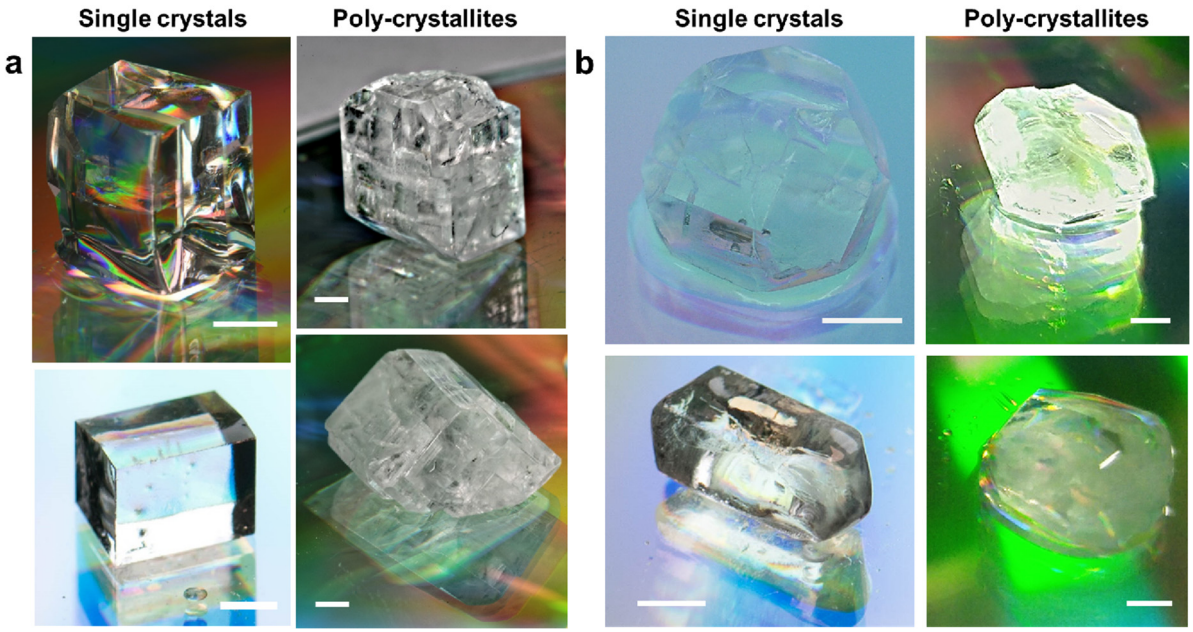


Fig. S4 Optical images of **(a)** single and polycrystalline CD-MOF-2 (Rb) crystals **(b)** single and polycrystalline CD-MOF-3 (Cs) crystal (Higher MeOH contents in diffusing contents preferentially give poly-crystallites). Scale bars correspond to 2 mm.

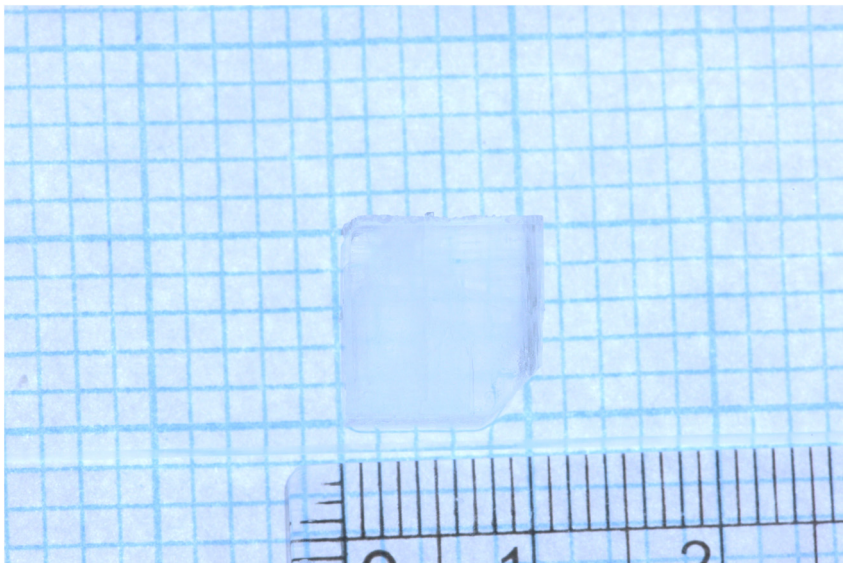


Fig. S5 A photograph of a CD-MOF-2 crystal placed onto a graduated paper and against a ruler. 1 cm size is clearly discernible.

Section 6. BET surface Area Analysis of N_2 gas sorption isotherms and pore size distribution of CD-MOF-2 (Rb) crystals

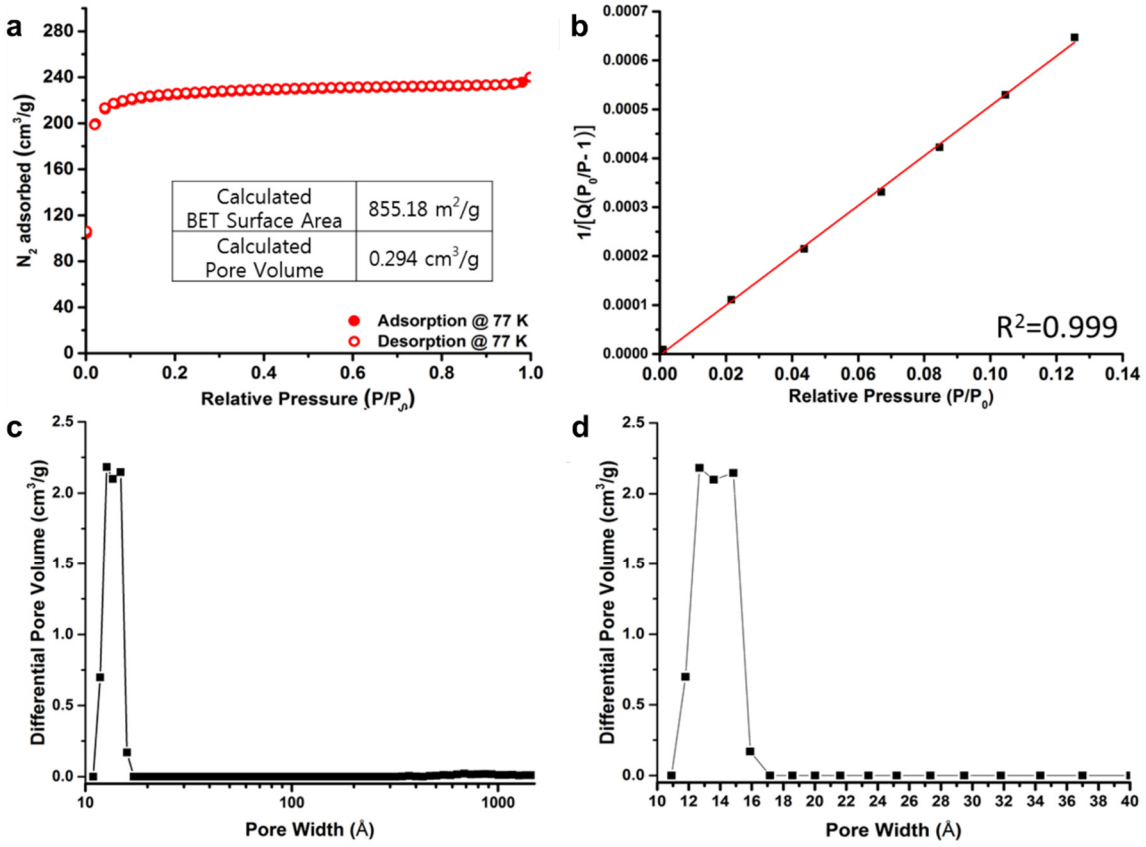


Fig. S6 (a) N_2 uptake isotherm and calculated BET surface area of CD-MOF-2 (Rb) crystallites. **(b)** BET plot for N_2 adsorption isotherm ($P/P_0 < 0.15$) **(c)** Pore size distribution in the range of 1-100 nm pore width (X axis is log scale). **(d)** Magnified pore size distribution in the range of 1-4 nm. (D_{pore} = 12-16 nm is comparable to ideal pore size of CD-MOF-2 (1.7 nm) and same as in the literature-reported analysis[S2])

Section 7. Phase diagrams of CD-MOF-2 (Rb) and CD-MOF-3 (Cs) single crystals and polycrystals

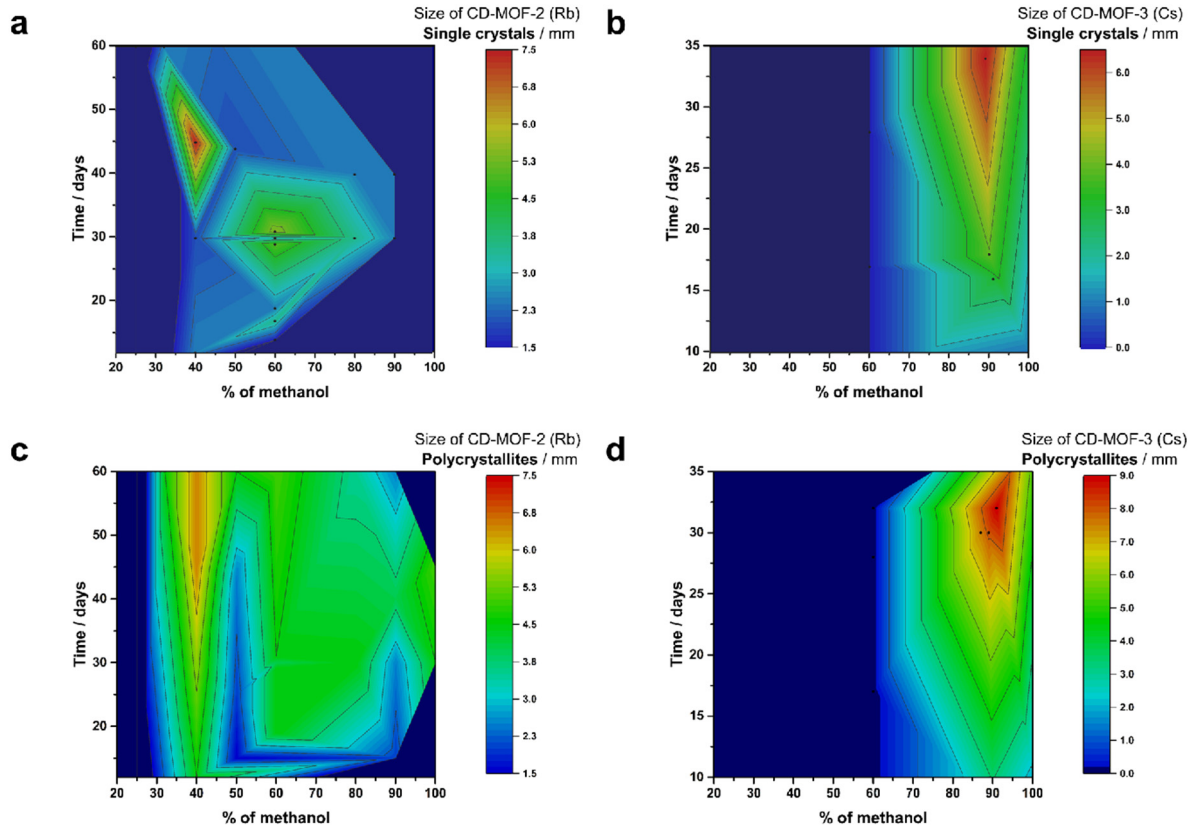


Fig. S7 *In situ* MOF crystallization studies (phase diagrams) of **(a)** single crystalline CD-MOF-2 (Rb), **(b)** CD-MOF-3 (Cs), **(c)** polycrystalline CD-MOF-2 (Rb), and **(d)** CD-MOF-3 (Cs) following crystallization time, percent of diffused methanol.

Section 8. Crystallographic Information of CD-MOF-4 (Cs) Crystals

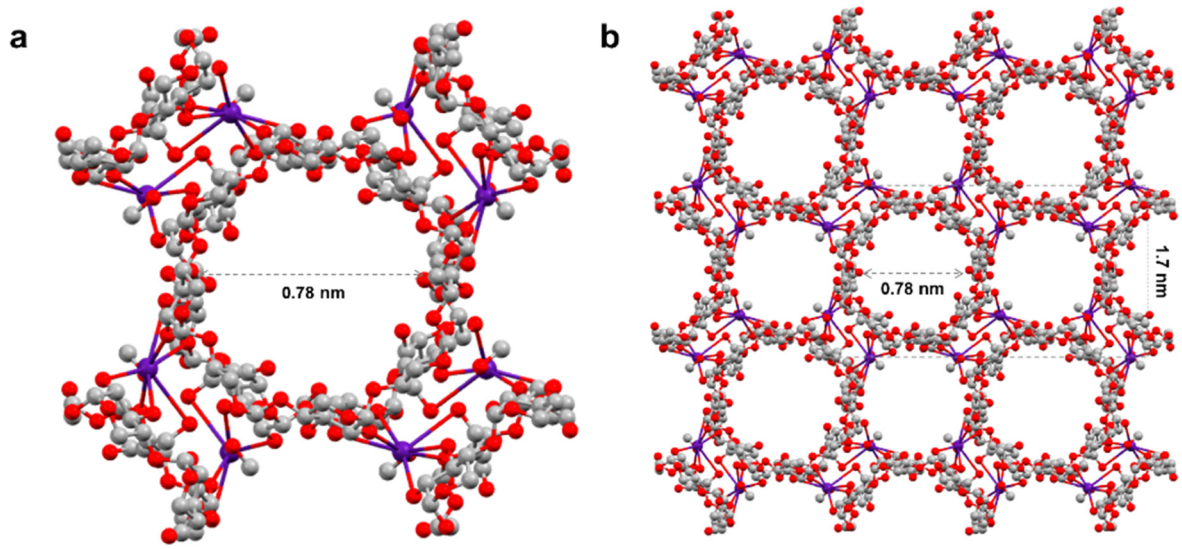
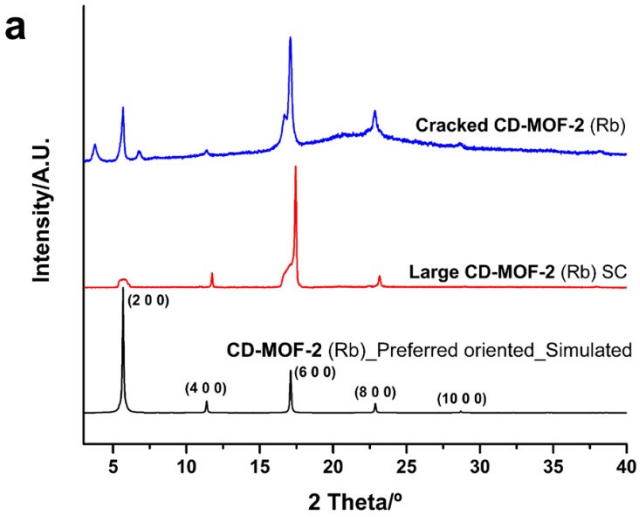
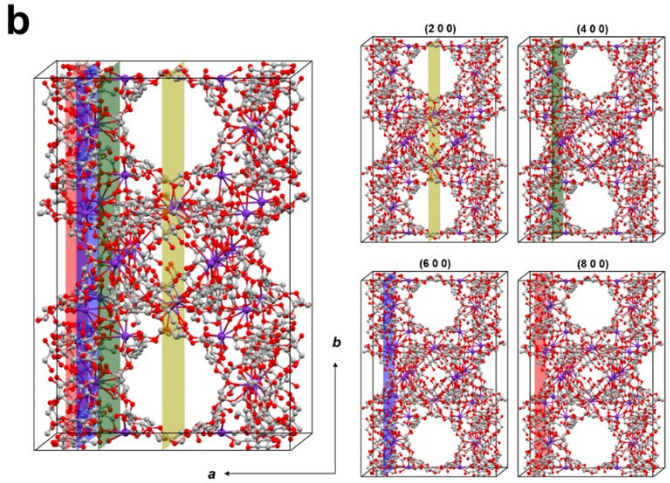


Fig. S8 (a) A unit cell of CD-MOF-4 (Cs) (a=b=24.136(6) Å, c=15.454(4) Å, α=β=γ 90º) crystals made from ɤ-CD and, respectively CsOH (red: oxygen; gray: carbon; purple: Cs). **(b)** One-dimensional porous channels in CD-MOF-4 (Cs) crystals (space group: I4; ccdc# 853695).

Section 9. Comment on relative intensities of the peaks characterizing preferentially-oriented single crystals.


a
Intensity/A.U.
Cracked CD-MOF-2 (Rb)
Large CD-MOF-2 (Rb) SC
(2 0 0)
CD-MOF-2 (Rb)_Preferred oriented_Simulated
(4 0 0)
(6 0 0)
(8 0 0)
(10 0 0)
5
10
15
20
25
30
35
40
2 Theta/°


b
(2 0 0)
(4 0 0)
(6 0 0)
(8 0 0)
b
a

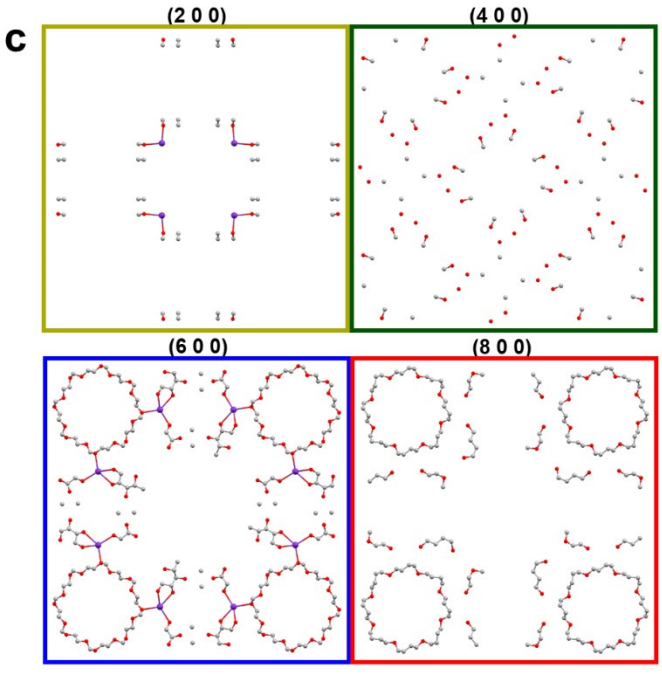

c
(2 0 0)
(4 0 0)
(6 0 0)
(8 0 0)

Fig. S9 (a) The PXRD pattern of large CD-MOF-2 (Rb) single crystals intact and after cracking. Simulated spectrum based on a unit cell of a single crystal is also shown and features different relative intensities of the peaks. This discrepancy is partly due to the effects of X-ray absorbance and penetration depth as well as the fact that calculated spectrum does not account for a specific orientation of the optical axis. **(b)** One-dimensional porous channels in CD-MOF-2 (Rb) with crystal planes (red: oxygen; gray: carbon; purple: Rb). **(c)** The atomic position of each plane.

Section 10. Optical images of intact, cracked, and grinded CD-MOF-2 (Rb) crystals.

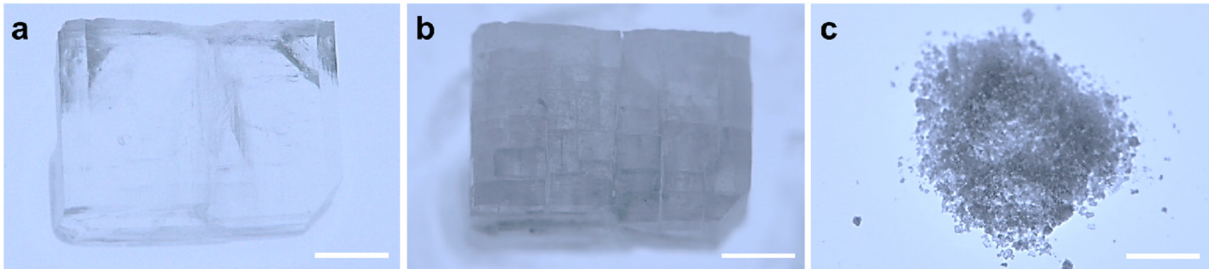


Fig. S10 Optical images of **(a)** single crystal of CD-MOF-2 (Rb) crystals, **(b)** cracked CD-MOF-2 (Rb) crystals, and **(c)** grinded CD-MOF-2 (Rb) crystals. Scale bars correspond to 2 mm.

Supplementary references:

[S1] Y. Wei, S. Han, D. E. Walker, P. E. Fuller and B. A. Grzybowski, *Angew. Chem. Int. Ed.*, 2012, **51**, 7435.

[S2] H. Li, M. R. Hill, R. Huang, C. Doblin, S. Lim, A. J. Hill, R. Babarao and P. Falcaro, *Chem. Commun.* 2016, **52**, 5973.