



High-yield, green and scalable methods for producing MOF-303 for water harvesting from desert air

Zhiling Zheng^{1,2,3}, Ha L. Nguyen^{1,2}, Nikita Hanikel^{1,2}, Kelvin Kam-Yun Li^{1,2}, Zihui Zhou^{1,2}, Tianqiong Ma^{1,2} and Omar M. Yaghi^{1,2,3}✉

Metal-organic frameworks (MOFs) are excellent candidates for water harvesting from desert air. MOF-303 (Al(OH)(PZDC), where PZDC is 1-*H*-pyrazole-3,5-dicarboxylate), a robust and water-stable MOF, is a particularly promising water-harvesting sorbent that can take up water at low relative humidity and release it under mild heating. Accordingly, development of a facile, high-yield synthesis method for its production at scale is highly desirable. Here we report detailed protocols for the green, water-based preparation of MOF-303 on both gram and kilogram scales. Specifically, four synthetic methods (solvothermal, reflux, vessel and microwave), involving different equipment requirements, are presented to guarantee general accessibility. Typically, the solvothermal method takes ~24 h to synthesize MOF-303, while the reflux and vessel methods can reduce the time to 4–8 h. With the microwave-assisted method, the reaction time can be further reduced to just 5 min. In addition, we provide guidance on the characterization of MOF-303, as well as water-harvesting MOFs in general, to ensure high quality of the product in terms of its purity, crystallinity, porosity and water uptake. Furthermore, to address the need for future commercialization of this material, we demonstrate that our protocol can be employed to produce 3.5 kg per batch with a yield of 91%. MOF-303 synthesized at this large scale shows similar crystallinity and water uptake capacity compared to the respective material produced at a small scale. Our synthetic procedure is green and water-based, and can produce the MOF within hours.

Introduction

Water scarcity is one of the greatest challenges facing society^{1,2}. The United Nations projects that almost five billion people will experience water stress by the year 2050 (ref. ³). Atmospheric water represents an alternative natural source of potable water with universal accessibility and availability in vast amounts. Indeed, there is six times as much water in the air at any time as in all freshwater rivers on our planet⁴. However, it is difficult to harvest atmospheric water directly because cooling air below its dew point is energy consuming, and this becomes even less favorable in drier climates (low relative humidity, RH), where it is most needed^{5–7}.

Fortunately, in recent years, the development of sorbent-assisted water-harvesting systems has made the extraction of drinking water from desert air more feasible. In this approach, the sorbent first captures the moisture from air and later releases concentrated water vapor upon minimal input of external power^{8–10}. Consequently, the water sorption properties and availability of suitable sorbents become critical to a wider application of the water-harvesting systems to address the water shortage¹¹. A desirable sorbent should have good water uptake capacity, fast kinetics at low RH, high energetic efficiency for capturing and releasing water, and long-term stability—all factors that need to be carefully assessed by an array of experiments, as demonstrated in previous studies^{8,12}. Additionally, synthetic scalability is crucial to allow the deployment of a promising sorbent candidate in household devices and become accessible to everyone^{13–15}.

As burgeoning candidates for sorbent-assisted water harvesting, metal-organic frameworks (MOFs) have attracted great interest owing to their intrinsic porosity, unprecedented variety and high tunability^{16,17}. However, with an overwhelming emphasis on the water uptake capacity and isotherm shape^{12,18–23}, most of the work on the discovery of suitable MOF sorbents is conducted on milligram

¹Department of Chemistry, University of California, Berkeley, CA, USA. ²Kavli Energy Nanoscience Institute, University of California, Berkeley, CA, USA. ³Bakar Institute of Digital Materials for the Planet, Division of Computing, Data Science, and Society, University of California, Berkeley, CA, USA. ✉e-mail: yaghi@berkeley.edu

or gram scale. Very few reports exist on kilogram-scale synthesis of MOFs relevant for water harvesting^{24–26}. Through a prototype demonstration in the Mojave Desert (35° N, 115° W), MOF-303 has been shown to be suitable for harvesting water from desert air⁸. Here we describe four different methods for making MOF-303 in high quality, at varying production scales and using green synthesis.

MOF-303 as a MOF that can be made using green synthetic methods

MOF-303 (Fig. 1) is constructed from one-dimensional infinite rod-like secondary building units (SBUs) that are connected by 1-*H*-pyrazole-3,5-dicarboxylate (PZDC) linkers. The combination of infinite rod SBUs and V-shaped linkers in MOF-303 generates the **xhh** topology²⁷. The reticular formula of MOF-303 is Al(OH)(PZDC)²⁸. Within the SBUs, each Al(III) ion is coordinated by two bridging hydroxyl groups and four carboxyl groups to form alternating *cis*–*trans* corner-shared AlO₆ octahedra (Fig. 1).

While there are certainly other MOFs that are scalable in synthesis and potentially suitable for water harvesting (Table 1)^{13,23,24,26,29–31}, one outstanding feature of MOF-303 production is that only water, a base, a metal salt and the linker molecule are used in a green, one-pot synthesis up to the kilogram scale.

Since these starting materials are soluble in basic water, they may potentially be recovered by means of an acid–base extraction or filtration upon acidification, and subsequently recycled, thus reducing the amount of waste generated during the MOF synthesis.

Compared with the traditional MOF synthesis protocols, this greener method, with water as the only solvent in the synthesis, is nondetrimental to human health and the environment by avoiding the use of toxic organic solvents. It should be noted that a few other aluminum-based MOFs listed in Table 1 also demonstrate promise for green synthesis, and our production methods can be potentially generalizable for the kilogram-scale synthesis of these materials as well.

In addition, in lieu of multistep organic synthesis and purification, the linker of MOF-303 is commercially available, which means that, in principle, its availability does not limit MOF-303 synthesis at scale.

Choice of synthetic approach

Considering the enormous potential of MOF-303 as a material for water harvesting and various other water-related applications^{8,32}, we sought to develop a comprehensive series of green and reliable synthetic approaches using different equipment to prepare this useful MOF. Particularly, we successfully increased the yield of MOF-303 production from 38% to 94% by slight modification of the reported aqueous-based reflux synthesis procedure for aluminum MOFs^{24,26,31,33}. The key parameter was the proportion of NaOH: increasing the molar equivalents from 1.5 to 3.0 was responsible for the improvement in yield. With the optimized 3:1 mole ratio between NaOH and H₂PZDC linker, the synthesized MOF-303 exhibits high crystallinity, as indicated by powder X-ray diffraction (PXRD) measurements (‘Procedure’). Moreover, the dramatic increase in the reaction yield inspired us to move forward to large-scale synthesis of MOF-303 based on the same approach (Table 2). We show that we can scale the synthesis to 3.5 kg per batch at homogeneous particle size with no compromises to its crystallinity and water uptake capacity (‘Anticipated results’).

Similarly, we also demonstrate that we can achieve a 1,000-fold increase in the space–time–yield via the reported microwave-assisted MOF-303 synthesis³⁴, and produce this material with high quality in minutes. The protocol also includes additional washing and drying procedures, which are critical to obtain the maximal porosity of MOF-303, especially in the large-scale synthesis.

Overall, we provide directions on the synthesis and purification of MOF-303 using green, scalable and reliable methods (Fig. 2). The four synthetic pathways described in Step 1 of the procedure are:

- Solvothermal (option A)
- Reflux (option B)
- Vessel (option C)
- Microwave (option D)

It is important to note that, although the synthetic procedures described in the methods were employed on a certain scale, they can also be easily scaled down with proper equipment for the given scale. This flexibility allows researchers to decide on the best method for MOF-303 synthesis based on their needs and instrumental availability. All the synthetic protocols are water based, and thus, they are safe and friendly to both researchers and the environment.

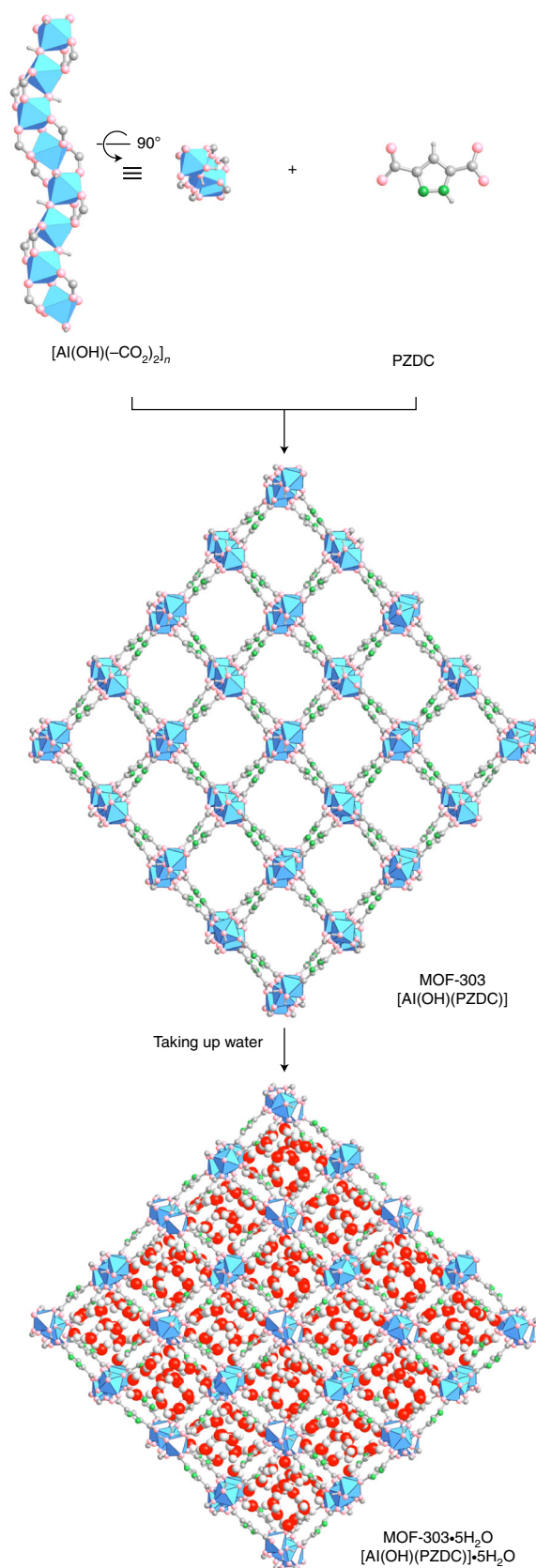


Fig. 1 | Crystal structure of MOF-303 constructed from infinite $[\text{Al}(\text{OH})(-\text{CO}_2)_2]_n$ rod SBUs stitched together by PZDC linking units. The crystal structure of MOF-303 filled with water is also presented.

Table 1 | Comparison of scalable synthesis methods of water-harvesting MOFs

| MOF | Solvent | Reaction time (h) | Dry MOF obtained per batch (kg) | Yield ^a (%) | Space-time-yield ^b (kg/m ³ /d) |
|--|--------------------------------|-------------------|---------------------------------|------------------------|--|
| MOF-303 | Water | 8 | 3.59 | 91 | 179.5 |
| CAU-10 (ref. ²⁴) | Water and ethanol | 10 | 0.5 | 93 | 137.7 |
| MIL-101 (ref. ²⁹) | Water | 15 | 0.13 | 68 | 84.6 |
| MIL-160 (ref. ³⁰) | Water | 24 | 0.014 | 93 | 185.3 |
| MOF-801 (ref. ²³) | Dimethylformamide | 12 | 0.01 | 86 | 74.1 |
| CAU-23 (ref. ³¹) | Water | 6 | 0.0045 | 84 | 137.1 |
| Al-fumarate ²⁶ | Water | 2.5 | 0.0004 | 74 | 358.1 |
| Ni ₂ Cl ₂ (BTDD) ¹³ | Dimethylformamide and methanol | 1 | 0.0002 | 80 | 12.2 |

^aYield of each MOF based on the amount of corresponding linkers. ^bQuantity of MOF produced per reaction volume in a given period of time.

Table 2 | Comparison of the four methods described in the procedure to synthesize MOF-303 [Al(OH)(PZDC)]

| Method of synthesis | Addition time (h) | Reaction time (h) | Reaction scale (mL) | $n_{\text{NaOH}}/n_{\text{linker}}$ | Yield ^b (%) | Mass of dry MOF per batch (g) | Production rate ^c (g/h) | Space-time-yield ^d (kg/m ³ /d) |
|---------------------|-------------------|-------------------|---------------------|-------------------------------------|------------------------|-------------------------------|------------------------------------|--|
| Solvothermal | 0.5 | 24 | 100 | 1.5 | 38 | 0.74 | 0.03 | 7.2 |
| Reflux | 2 | 2 | 100 | 3.0 | 94 | 1.87 | 0.47 | 112.2 |
| Vessel | 2 | 6 | 60,000 | 3.0 | 91 | 3,590 | 449 | 179.5 |
| Microwave | N/A | 0.1 | 15 | 3.0 | 92 | 0.54 | 5.4 | 8,640 |

^aMole ratio between NaOH and linker. ^bYield of Al(OH)(PZDC) based on the amount of linker H₂PZDC·H₂O. ^cMass of dry MOF product per hour. ^dQuantity of MOF produced per reaction volume in a given period of time.

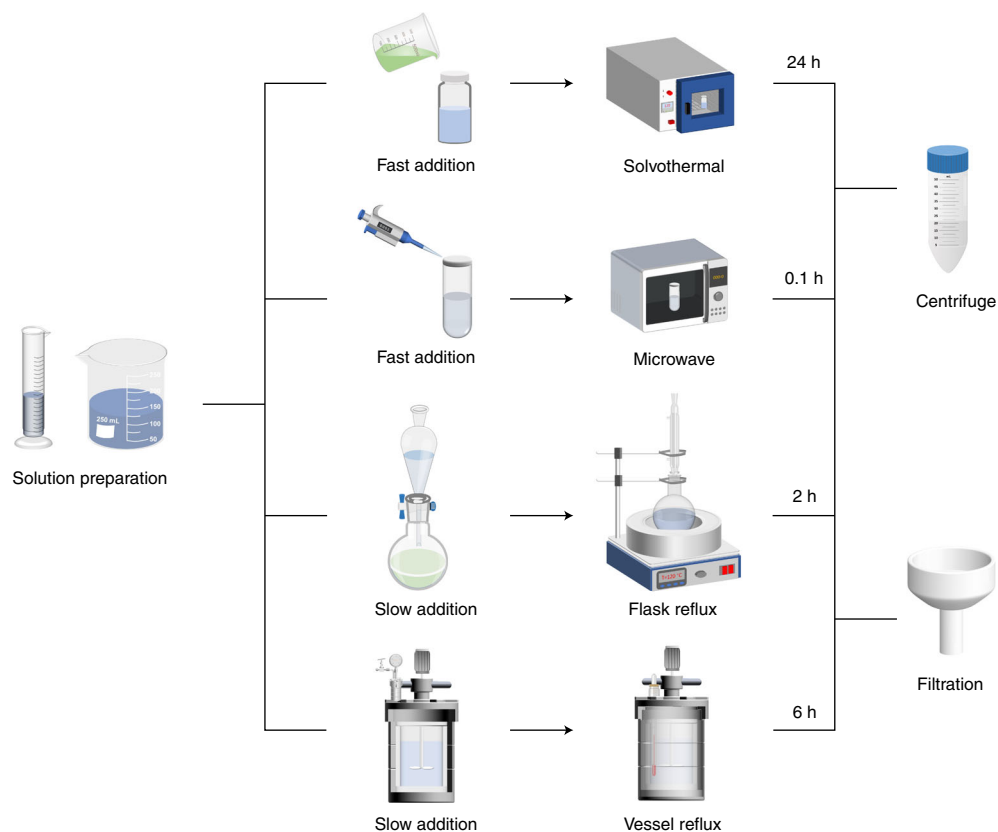


Fig. 2 | Various methods for the synthesis of MOF-303 along with the reaction time of each. Fast addition refers to immediate addition of the AlCl₃ solution to the linker solution (<1 min) in Step 1A(iv) and 1D(iv), and slow addition refers to dropwise addition of the AlCl₃ solution to the linker solution (~2 h) in Step 1B(iv) and 1C(viii).

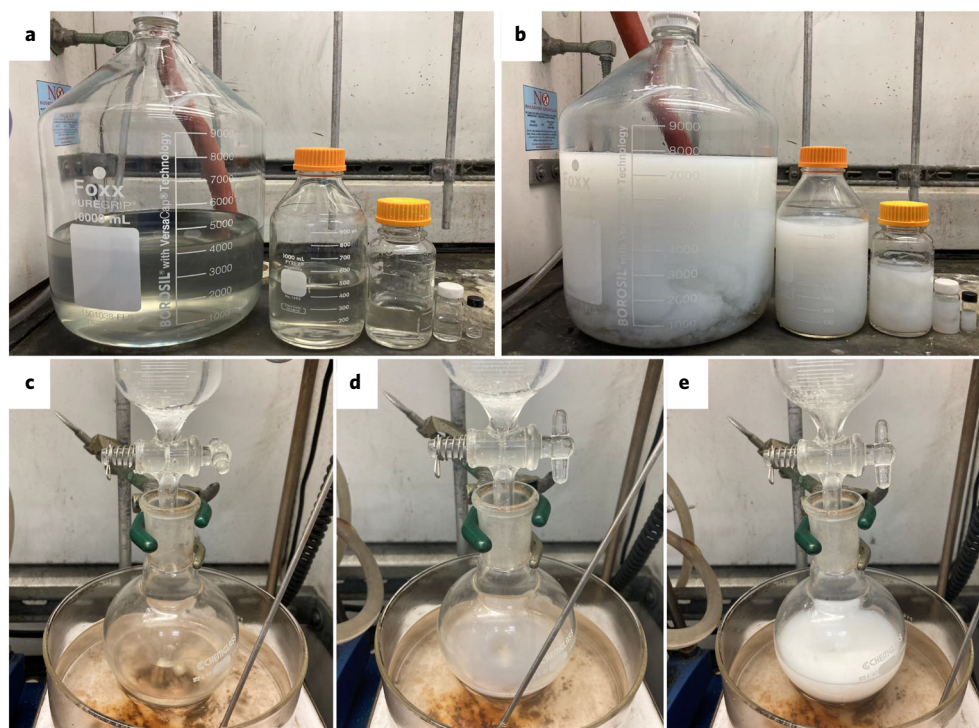


Fig. 3 | Equipment setup for MOF-303 synthesis. a,b, Hydrothermal synthesis in 4 mL, 20 mL, 250 mL, 1,000 mL and 10,000 mL containers before (a) and after (b) quick addition of AlCl_3 solution in Step 1A. **c–e**, Observation of the reaction in a 250 mL round-bottom flask after 10 mL (c), 20 mL (d) and 50 mL (e) of the AlCl_3 solution is slowly added to 50 mL of a colorless aqueous solution containing the organic linker in Step 1B.

Solvothermal

Of the four synthetic pathways, the solvothermal method has the fewest steps and the lowest instrumental requirement and is the easiest one to perform (the reaction is performed in a glass bottle placed inside an oven at 120 °C). Generally, the solvothermal synthesis of MOF-303 is applicable for reactions at milligram and gram scales, in which the reaction volume can range from 10 mL to 10,000 mL (Fig. 3). Before scaling up to larger reaction volumes, it is recommended to get familiar with the procedure at smaller, easier-to-handle scales to achieve the best quality of MOF-303. The procedure describes how to synthesize MOF-303 on a 750 mg scale in a 250 mL VWR bottle. At 38%, this approach has the lowest yield of the four methods.

Flask reflux

The flask reflux method has the highest reaction yield (94%, based on linker), which coupled with the much shorter reaction time (2 h) results in a more than 15-fold improvement of the space–time–yield. This approach method is scalable to reaction volumes ranging from 10 mL to 5,000 mL (to yield 0.1–500 g of MOF-303). Before scaling up to larger reaction volumes, it is recommended to get familiar with the procedure at smaller, easier-to-handle scales to achieve the best quality of MOF-303. Option C describes how to synthesize MOF-303 on a 2 g scale in a 250 mL round-bottom flask.

It is challenging to produce MOF-303 on kilogram scale using this method as the size of the flask will limit the reaction volume. For large-scale reactions with volumes of >5,000 mL, it is better to use the vessel reflux approach.

Vessel reflux

Vessel synthesis as described in option C, is designed for pilot-scale MOF-303 synthesis with reaction volumes >10 L. It is recommended to use 20 L, 50 L, 100 L or 200 L reaction vessels equipped with a condenser to run the reactions and adjust the reaction volumes accordingly. The vessel reflux method allows for high yield and production rate, which can be utilized for mass production of MOF-303. However, it can be time consuming to wash a large amount of product—a process that takes longer than the synthesis itself.

Microwave-assisted method

As for the microwave-assisted method, it is outstanding for the ultrahigh space–time–yield and the capability to produce MOF-303 with high quality in minutes, yet it relies heavily on the microwave synthesizer. It offers the easiest control over the particle size as well as the shortest preparation time (reactions usually complete within minutes). It is recommended for small-scale synthesis (100 mg to 10 g).

The reaction time may vary between 1 min and 10 min, depending on the model of the microwave reactor. If in doubt, we recommend initially using longer reaction times to ensure the completion of the reaction during the first trials. The reaction times can be gradually optimized by verifying the crystallinity of the products through the use of PXRD.

Washing and drying the product

Step 2 of the procedure provides two methods for washing the product. The first method involves centrifugation to obtain the solid product and is recommended for processing small-scale syntheses (10–1,000 mL reaction mixture). The second method requires vacuum filtration and is applicable to all reaction volumes, including large-scale syntheses with >30 L of solvent. Step 3 provides two methods for drying the product, either on a small scale (<1 kg) or a larger scale (>1 kg), depending on the amount of product you have and the degree of aggregation you expect.

Product characterization

In Step 4 we provide guidelines on how to perform some of the key characterization methods we use in our lab. While there is no particular preference for any one specific characterization method, we recommend that at least PXRD patterns (option A) should be collected to confirm crystallinity of the product before further characterization. Measurement of nitrogen isotherms (option B) and water isotherms (option C) provides additional information about the porosity and purity of the products. In addition, the working capacity can be extracted from the water sorption isotherms.

Scanning electron microscopy (SEM) imaging can be used to evaluate the morphology of the product and the particle size distribution. Digest-¹H NMR can be used to confirm the presence of the MOF's linker starting material and any organic impurities. The existence of impurities can also be determined by elemental analysis (option E), while thermogravimetric analysis (TGA; option F) might indicate if any defects are present in the MOF structure.

Materials

Reagents

! CAUTION It is essential to wear personal protective equipment and work in a well-ventilated lab and workspace to perform the syntheses.

- 1-*H*-pyrazole-3,5-dicarboxylic acid monohydrate, 97% (Aaron Chemicals, cat. no. AR0030FZ)
▲ CRITICAL Depending on the supplier and/or batch, the linker 1-*H*-pyrazole-3,5-dicarboxylic acid monohydrate might vary substantially in purity. If reactions give lower-crystallinity products, consider first relaunching the reaction using the linker from a different supplier or batch with higher purity.
- Aluminum chloride hexahydrate, 99% (AK Scientific, cat. no. 5468AF) **! CAUTION** Reagent is corrosive and can cause health issues if in contact with skin or eyes or if inhaled. Use protective clothes, gloves and eyewear at all times when handling.
- Sodium hydroxide, pellets, 98% (AK Scientific, cat. no. 0985AP) **! CAUTION** NaOH is a strong base and can cause skin burns. Personal protective equipment must be worn during experiments involving NaOH. In addition, solid NaOH is hygroscopic, which means it absorbs moisture from the atmosphere. Once it has a little moisture, carbon dioxide present in air can also be absorbed. To keep the mass reading correct, it is recommended that the weighing should be done within 5 min. Given the large quantities involved in these syntheses, the dissolution of large amount of NaOH in water must be handled with care.
- Ethyl alcohol (Sigma-Aldrich, cat. no. 493546)
- Deionized water (University of California, Berkeley)
- Deuterium oxide (Cambridge Isotope Laboratories, cat. no. DLM-6-10×1)
- Sodium deuterioxide, 30% in D₂O (Cambridge Isotope Laboratories, cat. no. DLM-57-50)
- Argon gas, industrial pure (Linde Gas & Equipment)
- Nitrogen gas, 99.999%, 5.0UH (Linde Gas & Equipment)

Equipment

- Spatula
- Magnetic stir bar
- Water condenser
- Mortar and pestle
- Hot plate (IKA, cat. no. 0003487001)
- Filter paper, 100 circles, 125 mm (Whatman, cat. no. 1001-125)
- Filter paper, 2 mm, 60 cm (USA Lab, cat. no. QUAL-2UM)
- Weighing balance (Mettler Toledo)
- Top loading balance (Sartorius)
- Vortex mixer (Corning LSE)
- Dram vial, 4 mL (Fisher Scientific)
- Scintillation vial, 20 mL (VWR International)
- Pyrex pressure reaction vessel with silicone cap, 35 mL (CEM, cat. no. 909036)
- Erlenmeyer flask, 100 mL
- Addition funnel, 100 mL
- Round-bottom flask, 250 mL
- Medium bottle, 250 mL (VWR International)
- Autoclavable borosilicate glass storage bottle, 10 L (United Scientific, cat. no. BM10000)
- Polypropylene beaker, 10 L (United States Plastic, cat. no. 76271)
- Glass feeding funnel, 15 L
- Glass reactor with heating jacket, 200 L (Across International)
- Discover SP microwave synthesizer (CEM)
- Centrifuge tube, 15 mL (VWR North American, cat. no. 89039-668)
- Centrifuge tube, 50 mL (VWR North American, cat. no. 89039-656)
- Wide-mouth HDPE centrifuge bottle with closure, 250 mL (Thermo Scientific, cat. no. 0331379D)
- Sorption tube, 12 mm (Micromeritics)
- Sorption tube, 9 mm (Anton Paar)
- Aluminum foil pan (1/2" × 10 1/4" × 2 1/2")
- Centrifuge 5810R (Eppendorf, 6 × 50 mL angle rotor, cat. no. 022628067)
- Centrifuge 5816 (Ohaus, 6 × 250 mL angle rotor, cat. no. 30314817)
- Centrifuge Z366 (Hermle, 6 × 250 mL angle rotor, cat. no. Z366)
- Isotemp oven (Fisher Scientific)
- Vacuum oven (VWR International)
- Sonicator (Branson)
- Vacuum filter, 20 L (USA Lab, cat. no. VACFILTER20L)
- Pump (Branson)
- Miniflex 600 powder X-ray diffractometer (Rigaku)
- Flash Smart Elemental analyzer (ThermoFisher)
- ASAP 2420 porosimetry and accelerated surface area system (Micromeritics)
- Vapor sorption analyzer, BELSORP-aqua3 (BEL Japan)
- Programmable Refrigerated Bath Isotemp 3016P (Fisher Scientific)
- FloVac six-port vacuum and flow degasser (Quantachrome)
- NEO-500 NMR spectrometer with Avance IV NEO console and a 5 mm 1H/BB iProbe (Bruker)
- Scanning electron microscope S-5000 (Hitachi)
- Thermal analysis system Q500 (TA instruments)

Procedure

- 1 In total, we present four methods for synthesizing MOF-303, aiming to satisfy varying demands and limitations by focusing on different aspects such as simplicity, high space–time–yield, reduced reaction time and large-scale production. Option A provides a method for the simple and easy synthesis of MOF-303 (0.1–10 g), while option B offers a high yield (>90%) and fast speed (<6 h total time) gram-scale synthesis of MOF-303 (1–10 g). A protocol for the large-scale synthesis of MOF-303 is detailed in option C (1–20 kg). Option D describes an ultrafast synthetic method of MOF-303 (<5 min). All four options are one-step syntheses. Fully washed and desolvated MOF-303 is stable in air at room temperature (RT, 20–25°C) for months and can be stored in either wet or dry environments. It is recommended to store MOF-303 in a sealed container away from low- or

high-pH environment and volatile chemicals. In some cases, activation or desolvation is needed to remove adsorbed water before use or characterization (for more information, see Step 4).

(A) **Solvothermal synthesis of MOF-303 (750 mg scale)** ● **Timing 26 h**

- (i) Add 0.6 g (0.015 mol) of NaOH and 1.74 g (10 mmol) of 1-*H*-3,5-pyrazoledicarboxylic acid monohydrate ($\text{H}_2\text{PZDC}\cdot\text{H}_2\text{O}$) to a 250 mL VWR bottle.

! CAUTION The size of the bottle should be at least 20% larger than the total volume of the solvent involved in the solvothermal synthesis. Limited head space can cause overpressure of the bottle during the reaction.

- (ii) Add 90 mL of deionized water to the bottle, and stir the solution (using a stir bar) to dissolve the solids.

▲ CRITICAL STEP It is important to make sure that aluminum chloride hexahydrate ($\text{AlCl}_3\cdot 6\text{H}_2\text{O}$) is completely dissolved in water, resulting in a clear and colorless solution.

- (iii) Into a separate 20 mL scintillation vial, add 2.41 g (10 mmol) of $\text{AlCl}_3\cdot 6\text{H}_2\text{O}$ and 10 mL deionized water to fully dissolve it.

- (iv) Add the $\text{AlCl}_3\cdot 6\text{H}_2\text{O}$ solution to the reaction mixture through an addition funnel while stirring at 100 rpm. White precipitates form halfway through the addition, and the resulting solution becomes milky white (Fig. 3).

- (v) Remove the stir bar from the reaction vessel, and tightly cap the bottle.

- (vi) Heat the reaction mixture in an Isotemp oven at 120 °C for 24 h.

- (vii) Cool down the reaction mixture to RT. It takes ~60 min for the hot reaction mixture to naturally cool down to RT. The MOF-303 product can be found as a white precipitate at the bottom of the bottle.

▲ CRITICAL STEP Make sure the cap is tightly closed. The reaction temperature is above the boiling point of water, and the solution can easily evaporate if the cap is loose. Let the reaction run for no less than 15 h, as incomplete reaction will result in a lower-quality product with reduced crystallinity and surface area. It is possible to let the reaction run for a longer time period (up to 72 h) without any negative effects on the product's quality, as long as the evaporation of water is avoided.

(B) **Reflux synthesis of MOF-303 (2 g scale)** ● **Timing 6 h**

- (i) Add 1.74 g (5 mmol) of $\text{H}_2\text{PZDC}\cdot\text{H}_2\text{O}$ and 1.2 g (30 mmol) of NaOH to a 100 mL Erlenmeyer flask.

▲ CRITICAL STEP The mole ratio between the linker and NaOH is critical to reach a high yield for the reflux synthesis. The yield will be dramatically reduced when deviating from a molar ratio of 3:1 (NaOH: H_2PZDC).

- (ii) Add 50 mL of deionized water to the flask, and stir the solution (using a stir bar) for 10 min to dissolve the solids. Transfer the solution to a 250 mL round-bottom flask.

? TROUBLESHOOTING

- (iii) In a separate 100 mL Erlenmeyer flask, prepare a solution of 2.41 g (30 mmol) of $\text{AlCl}_3\cdot 6\text{H}_2\text{O}$ in 50 mL of deionized water. Stir the solution (using a stir bar) for 10 min or use sonication for 5 min to dissolve the solids.

- (iv) Use a 100 mL addition funnel to add the AlCl_3 solution dropwise at 1 mL/min to the reaction vessel while stirring at 200 rpm at RT. The addition process lasts for 2 h. White precipitate forms halfway through the addition and the reaction mixture becomes cloudy (Fig. 3).

▲ CRITICAL STEP The addition rate should be as slow as possible. Make sure that the magnetic stir bar in the round-bottom flask is constantly stirring during the addition. The particle size of the product will be affected by the rate of the addition, with slower addition rates resulting in high-quality products. The failure to add the solution at a rate slower than 1 mL/min may result in a substantial hysteresis in the water vapor isotherm of the synthesized products.

- (v) Heat the reaction mixture to 120 °C using an oil bath under reflux for 2 h.

▲ CRITICAL STEP The reaction mixture becomes more and more cloudy as the temperature increases. It is important to reach 100 °C, the boiling point of water, in ~10 min to avoid the formation of low-crystallinity MOF-303. This can be achieved by applying the full heating power of the heat plate or placing the flask in a preheated 120 °C oil bath. The magnetic stir bar should be constantly stirring to make sure the reaction mixture is being heated homogeneously.



Fig. 4 | A 3-kg-scale synthesis of MOF-303 in a 200 L reaction vessel. a, Reaction setup of the vessel equipped with an addition funnel, a condenser and an overhead rotor connected with a spinner. **b**, Formation of a white precipitate after refluxing for 6 h.

- (vi) Cool down the reaction mixture to RT. It takes ~60 min for the hot reaction mixture to naturally cool down to RT. The MOF-303 product can be found as a white precipitate at the bottom of the flask.

? TROUBLESHOOTING

(C) Vessel synthesis of MOF-303 (3.5 kg scale) ● Timing 10 h

▲ **CRITICAL** This option is designed for pilot-scale MOF-303 synthesis with reaction volumes >10 L. It is recommended to use 20 L, 50 L, 100 L or 200 L reaction vessels equipped with a condenser to run the reactions and adjust the reaction volumes accordingly. Herein, we describe steps to synthesize MOF-303 on a 3.5 kg scale in a 200 L reaction vessel (Fig. 4a).

- (i) To a 200 L reaction vessel, add 45 L of deionized water at RT.
 (ii) Add 2.4 kg (60 mol) of NaOH to the reactor slowly through the material-feeding port with the spinner stirring at 100 rpm.
 (iii) Add 3.48 kg (20 mol) of H₂PZDC·H₂O to the reactor slowly through the material feeding port.

! **CAUTION** Monitoring the temperature of the reaction mixture during the addition of the linker is required, as this step also releases heat when the linker is deprotonated by the base. If the temperature rises above 60 °C, stop adding the linker and wait for the mixture to cool down naturally.

▲ **CRITICAL STEP** The mole ratio between the linker and NaOH is critical to reach a high yield for the synthesis. The yield will be dramatically lower when deviating from a molar ratio of 3:1 (NaOH:H₂PZDC).

- (iv) Stir the reaction mixture for 30 min until the linker is fully dissolved, which is indicated by a clear solution.

? TROUBLESHOOTING

- (v) In two or three 10 L plastic beakers, weigh out a total of 4.82 kg (20 mol) of AlCl₃·6H₂O in all beakers combined, and add a total of 15 L of deionized water to the beakers.
 (vi) Stir the solution using a magnetic stir bar for 10 min to fully dissolve AlCl₃·6H₂O.
 (vii) Transfer the solutions in the beakers to a 15 L feeding funnel.
 (viii) Add the solution slowly to the reaction mixture at ambient conditions while stirring. Adjust the addition speed by turning the valve on the addition funnel so that the total addition time is no less than 2 h. The recommended addition rate is ~125 mL/min. Halfway through the addition, a white precipitate forms and the solution in the reaction vessel becomes milky (Fig. 4b).

▲ CRITICAL STEP The amount of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ added to the reaction mixture in this procedure is important to reach a high yield and avoid the formation of undesirable byproducts. Make sure that the $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ is fully dissolved and transferred to the feeding funnel. If necessary, add 500–1,000 mL of deionized water to completely dissolve the remaining solids at the bottom of the beaker. The addition should be as slow as possible to obtain MOF-303 with large particle sizes.

- (ix) While stirring vigorously, heat the reaction mixture to 120 °C by a heating jacket and reflux for 6 h.

! CAUTION The temperature of the water vapor is ~100 °C and can easily burn your skin. Examine all the ports, and make sure they are closed except the vent on the condenser. It is recommended to monitor the pressure within the vessel by a pressure gauge.

▲ CRITICAL STEP The reaction mixture becomes cloudier as the temperature gets closer to 100 °C, which is an indication of the formation of MOF-303.

- (x) Cool down the reaction mixture to RT. It takes ~90 min for the hot reaction mixture to naturally cool down to RT. The MOF-303 product can be found as a white precipitate at the bottom of the vessel.

? TROUBLESHOOTING

(D) **Microwave synthesis of MOF-303 (1 g scale) ● Timing 30 min**

- (i) Add 522 mg (3 mmol) of $\text{H}_2\text{PZDC} \cdot \text{H}_2\text{O}$ and 360 mg (9 mmol) of NaOH to a 20 mL scintillation vial.

▲ CRITICAL STEP The mole ratio between the linker and NaOH is critical to reach a high yield for the reflux synthesis. The yield will be dramatically reduced when deviating from a molar ratio of 3:1 (NaOH: H_2PZDC).

- (ii) Add 12 mL of deionized water to the vial, and stir the solution using a stir bar for 10 min to dissolve the solids.

? TROUBLESHOOTING

- (iii) In a separate 20 mL scintillation vial, prepare a solution of 723 mg (3 mmol) of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ in 3 mL of deionized water.

- (iv) Transfer the solutions from both vials to a 35 mL Pyrex pressure reaction vessel. The solution becomes cloudy immediately after the liquids are mixed.

- (v) Place a $0.375 \times 0.5''$ magnetic stir bar into the Pyrex pressure reaction vessel, and seal the vessel with a silicone cap.

- (vi) Heat the reaction mixture to 120 °C at 300 W while stirring in a microwave reactor for 5 min.

▲ CRITICAL STEP The reaction time may vary between 1 min and 10 min, depending on the model of the microwave reactor. If in doubt, it is recommended to initially use longer reaction times to ensure the completion of the reaction during the first trials. The reaction times can be gradually optimized by verifying the crystallinity of the products through the use of PXRD.

- (vii) Cool down the reaction mixture to RT. It takes ~20 min for the hot reaction mixture to naturally cool down to RT. The MOF-303 product can be found as a white precipitate at the bottom of the vial.

- 2 There are two options for washing the crude MOF-303 products. Option A is recommended for washing the reaction products from small-scale MOF-303 syntheses (10–1,000 mL). Nevertheless, it is possible to wash up to 20 kg by following option A and repeating the procedure multiple times using larger centrifuge containers. Option B requires less time than other methods and is easier to follow when the reaction volume exceeds 30 L. Therefore, it is recommended for large-scale MOF-303 syntheses.

(A) **Centrifugation method ● Timing 30 min**

▲ CRITICAL Here we describe a procedure to wash ~2 g of MOF-303 from a 100 mL reaction mixture using 50 mL centrifuge tubes. Depending on the actual reaction volume you are running, it is possible to use 15 mL, 250 mL, 500 mL and 1,000 mL centrifuge tubes or bottles instead, and adjust the amount of washing solvents accordingly (Fig. 5a).

- (i) Transfer the 100 mL reaction mixture to 4×50 mL capped centrifuge tubes (25 mL in each tube).

- (ii) Separate the solids by centrifugation at 6,050g for 1 min at RT.

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Fig. 5 | Purification of MOF-303 at 3 kg scale. **a**, Centrifugation with 250 mL open-mouth bottles and drying in the hood. **b**, 20 L filtration funnel. **c**, Filtering 10 L of crude MOF-303 reaction mixture. **d**, White MOF solids obtained after the filtration. **e**, Collecting 3 kg of MOF powder in aluminum foil pans. **f**, Grinding aggregates into a fine powder.

- (iii) Discard the supernatant, and add 40 mL of deionized water to each tube.
 - **PAUSE POINT** The as-synthesized MOF-303 is stable in water and organic solvents. It can be stored at ambient conditions for months without any negative impact on its quality. It is useful to note that MOF-303 can be soaked in water or ethanol (or other organic solvents such as acetone or methanol) without reducing its quality. The readers can choose to pause at any point after they decant the mother liquid/ supernatant (which is slightly basic and slowly digests MOF-303) in Step 2(iii). Although MOF-303 is stable in both air and most pH-neutral liquids, at this point (before Step 2(iv)), the washing of MOF-303 is not finished yet, so soaking in water can save the reader's time and they can do the next run of centrifuge when they return to the experiment.
- (iv) Place the tube on a vortex mixer, and shake the mixture until the solids are homogeneously dispersed in deionized water to form a milky solution.
 - ▲ **CRITICAL STEP** This washing step serves to remove aluminum chloride and sodium chloride remaining in the product. Be sure to wash the solids thoroughly with the deionized water to fully dissolve and remove the salts.
- (v) Repeat the washing process in Step 1D(iii–iv) two additional times.
 - **PAUSE POINT** The water-washed MOF-303 can be stored at ambient conditions for months without any negative impact on its quality.
- (vi) In each centrifuge tube, soak the MOF in 40 mL of anhydrous ethanol (EtOH). Use a vortex to fully mix the washing solvent and MOF.
 - ▲ **CRITICAL STEP** This washing step serves to remove impurities such as unreacted linker molecules within the pores of the MOF. Be sure to fully mix ethanol with the solids.
- (vii) Separate the solids by centrifugation at 6,050g for 2 min, and discard the supernatant.

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- (viii) Repeat the ethanol washing process in Step 1D(vi–vii) two additional times.
 - **PAUSE POINT** The ethanol-washed MOF-303 can be stored at ambient conditions for months without any negative impact on its quality.
- (ix) Dry the washed MOF-303 under air overnight to obtain the crude product.
- (B) **Filtration method** ● **Timing 12 h**
 - ▲ **CRITICAL** Here we describe a procedure for washing 1 kg of MOF-303 from a 10 L reaction mixture using a 20 L filter (Fig. 5b). Depending on the actual reaction volume you are running, it is possible to divide the reaction mixture into multiple parts to be subsequently washed.
 - (i) Pour the 10 L reaction mixture into a 20 L stainless steel vacuum filter equipped with a 2 mm filter paper to remove the mother liquor by vacuum filtration (Fig. 5c).
 - ▲ **CRITICAL STEP** A thick layer of white precipitate can accumulate quickly on the filter, thus slowing down the filtration process. Add the solution slowly, and use a spatula frequently to stir the solution. This can greatly reduce the waiting time. Be sure to check that all parts in the filtration system are sealed.
 - (ii) Add 20 L of deionized water to the funnel to wash the collected MOF by vacuum filtration.
 - **PAUSE POINT** The water-washed MOF-303 can be stored at ambient conditions for months without any negative impact on its quality. At this point, it will be mostly wet powder (with a little amount of water left behind in the funnel). In either case (dry or under water), MOF-303 is stable and ready for the next step.
 - (iii) Dry the precipitate under ambient conditions for 2 h, and transfer the obtained solids to a 10 L plastic beaker.
 - (iv) In a 10 L glass reservoir bottle, add 4 L of anhydrous EtOH and place it in an oven at 70 °C for 30 min.
 - ! **CAUTION** The size of the bottle should be at least 20% larger than the total volume of EtOH for the heating step. Limited head space can cause overpressure and potential explosion of the bottle.
 - (v) Transfer the hot EtOH to the plastic beaker, and stir the mixture using a magnetic stir bar for 5 min.
 - ! **CAUTION** This step must be handled in the hood. A large amount of ethanol vapor may be explosive.
 - ▲ **CRITICAL STEP** Be sure to mix MOF thoroughly with the hot EtOH. This step serves to remove the unreacted linker molecules as well as the linker molecules that might be trapped in the pores of MOF. This is critical to obtain MOF-303 with a desirable surface area and water uptake performance.
 - (vi) Pour the mixture back to the 20 L filter, and remove the solution by vacuum filtration.
 - **PAUSE POINT** The ethanol-washed MOF-303 can be stored at ambient conditions for months without any negative impact on its quality.
 - (vii) Repeat Step 2B(iii–vi) once again.
 - (viii) Dry the precipitate under ambient conditions for 2 h (Fig. 5d).
- 3 There are two options for drying MOF-303, which depend on the scale of the reaction. In general, aggregation of the solids can be observed during the large-scale MOF production, and extra care should be taken to grind the aggregates into a fine powder for further use. Follow option A for drying <1 kg MOF with minimal amounts of aggregates. Follow option B for drying >1 kg MOF with substantial amounts of aggregates. In our experience, there is very little aggregation in the <1 kg reaction. While the product might appear aggregated at first, the small ‘bricks’ break down naturally, as water is lost. Therefore, the key difference here is to use a mortar (small scale) or a machine (large scale) to mill/grind the product.
 - (A) **Drying MOF-303 at 30 g scale** ● **Timing 3 h**
 - (i) Place the centrifuge tubes containing MOF into a vacuum oven at 80 °C for 2 h.
 - ? **TROUBLESHOOTING**
 - (ii) Cool the MOF to RT.
 - **PAUSE POINT** The dried MOF-303 can be stored at ambient conditions for months.
 - (iii) Use a mortar to grind the white aggregates.
 - (B) **Drying MOF-303 at 3 kg scale** ● **Timing 25 h**
 - (i) Transfer the white solids to a 1/2" × 10 1/4" × 2 1/2" aluminum foil pan, and place in an oven at 120 °C for 24 h (Fig. 5e).
 - (ii) Remove the pan with MOF from the oven, and cool the MOF to RT.
 - **PAUSE POINT** The dried MOF-303 can be stored at ambient conditions for months.

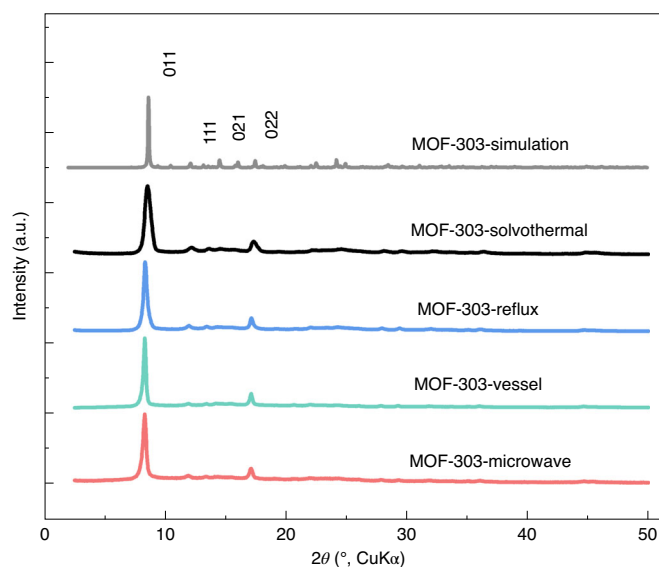


Fig. 6 | PXRD patterns of MOF-303 synthesized by different methods. The simulated pattern (gray) was overlaid with the experimental patterns from the solvothermal method (black), reflux method (blue), vessel method (green) and microwave method (red).

- (iii) In a stainless swing spice grinder, place 500 g of white solid and grind at 25,000 rpm for 5 s (Fig. 5f).
- (iv) Repeat Step 3B(iii) six times, and collect the white powder.

General procedure for MOF characterization

- 4 To determine the quality of MOF-303, we present several options to characterize the product. Though there is no preference toward one specific method, it is recommended that at least PXRD patterns (option A) should be collected to confirm crystallinity of the product before other characterizations. Measurement of nitrogen isotherms (option B) and water isotherms (option C) give further indication about the porosity and purity of the products. Digest-¹H NMR can be used to confirm the presence of the MOF's linker starting material and any organic impurities. The existence of impurities can also be determined by elemental analysis (option E), while TGA (option F) might indicate if any defects are present in the MOF structure. SEM can be used to evaluate the morphology and particle distribution of the synthesized MOF-303 samples.

(A) Collecting PXRD data ● Timing 15 min

- (i) Transfer ~5 mg of dried MOF-303 onto a clean zero-diffraction silicon sample holder.
- (ii) Use a spatula to pack the powder densely onto the surface of the sample holder.
- (iii) Using a Rigaku Miniflex 600 diffractometer (Bragg-Brentano geometry, Cu K α radiation), scan the diffraction pattern between 2° and 50° with 0.02° steps at a collection speed of 4° per min (Fig. 6).

We note that alternative instrumentation (e.g., Bruker D8 Advance X-ray diffractometer) could be utilized for the PXRD analysis in a similar manner.

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(B) Collecting nitrogen isotherm data ● Timing 12 h

- (i) Transfer ~100 mg of dried MOF-303 into a preweighed sorption cell (Micromeritics), which is filled with argon gas.
- (ii) At the degassing station of the ASAP 2420 system, heat the cell at a rate of 0.5 °C/min to reach 120 °C and hold at this temperature for 6 h under dynamic vacuum. Track the pressure reading on the instrument throughout the activation procedure, and make sure that a minimal pressure value is achieved at the end of the activation, thus indicating complete desolvation of the MOF.

▲ CRITICAL STEP The MOF sample must be fully activated. Incomplete activation of the sample will compromise the measurement results.

- (iii) Cool the sorption tube to RT, and refill with argon gas.
- (iv) Record the weight of the activated MOF-303.

- (v) Place the sorption tube with an isothermal heating jacket at the analysis station of the ASAP 2420 system, and record the nitrogen isotherm between $P/P_0 = 0$ and $P/P_0 = 0.99$ at 77K. **▲ CRITICAL STEP** Collecting more data points between $P/P_0 = 0$ and $P/P_0 = 0.10$ can give a more accurate estimation of the Brunauer–Emmett–Teller (BET) specific surface area and pore size distribution.

- (vi) Analyze the collected data with the Microactive software from Micromeritics.

We note that alternative instrumentation (e.g., QUADRASORB evo Gas Sorption Surface Area and Pore Size Analyzer from Anton Paar) could be utilized for the nitrogen sorption analysis in a similar manner, which would, however, require the use of a different software package (provided by Anton Paar) for data analysis.

(C) Collecting water isotherm data ● Timing 72 h

- (i) Transfer ~50 mg of dried MOF-303 into a preweighed sorption tube (Anton Paar), which is filled with argon gas.
- (ii) In a degasser, heat the sample to 120 °C under vacuum for 6 h. Track the pressure reading on the instrument throughout the activation procedure, and make sure that a minimal pressure value is achieved at the end of the activation, thus indicating complete desolvation of the MOF.
- (iii) Cool the sorption tube to RT, and refill with argon gas.
- (iv) Record the weight of the activated MOF-303.
- (v) Before the measurement, degas the water vapor source through five freeze–pump–thaw cycles. For this purpose, freeze the vapor source with liquid nitrogen and apply vacuum for 5 min. Turn off the vacuum, and let the vapor source thaw at 40 °C. Repeat this process four more times.
- (vi) On a BEL Japan BELSORP-aqua3, measure the water vapor sorption isotherm at 25 °C. Use ultra-high purity helium gas for the free space correction conducted by the instrument during the measurement. Additionally, use an isothermal bath (e.g., Programmable Refrigerated Bath Isotemp 3016P) to adjust the analysis temperature.

We note that alternative instrumentation (e.g., vapor sorption volumetric gas sorption analyzer Vstar from Anton Paar) could be utilized for the water sorption analysis in a similar manner.

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(D) Conducting digest-¹H-NMR spectroscopy experiments ● Timing 10 min

- (i) Transfer ~10 mg of dried MOF-303 into a 4 mL dram vial.
- (ii) Add 1 mL of D₂O followed by 0.1 mL of 30 wt% NaOD in D₂O solution to the vial.
- (iii) Sonicate the mixture for 5 min to obtain a colorless clear solution.
- (iv) Transfer the solution into an NMR tube, and record the ¹H-NMR spectrum (Fig. 7).

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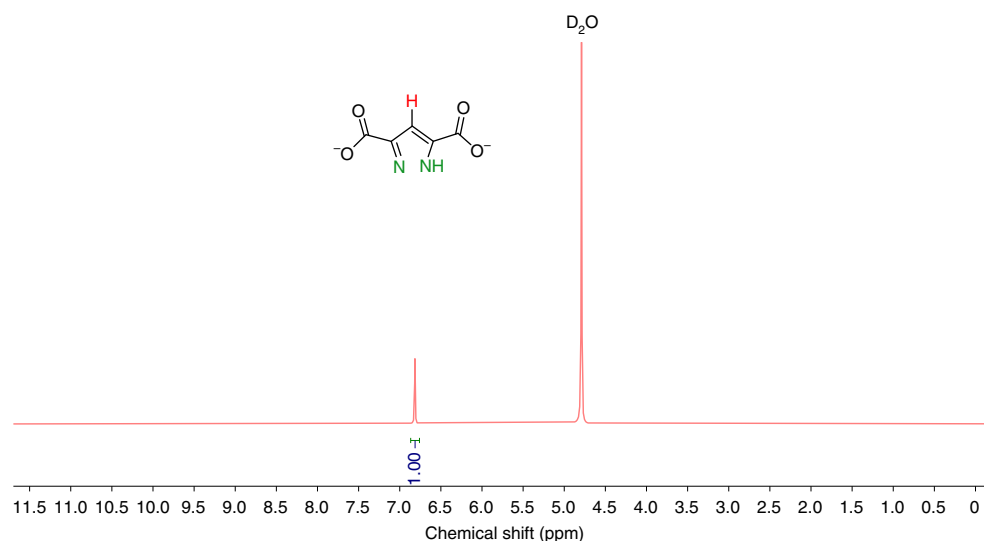


Fig. 7 | Solution-state ¹H-NMR spectrum of the fully base-hydrolyzed MOF-303. The sample has been thoroughly washed with EtOH and dried before its digestion.

(E) Collecting elemental microanalysis data ● Timing 8 h

- (i) Transfer ~20 mg of dried MOF-303 into a sorption tube.
- (ii) At the degassing station of the ASAP 2420 system, heat the tube at a rate of 2.0 °C/min to reach 120 °C and hold at this temperature for 6 h. Track the pressure reading on the instrument throughout the activation procedure, and make sure that a minimal pressure value is achieved at the end of the activation, thus indicating complete desolvation of the MOF.
- (iii) Cool the sorption tube to RT, and transfer the tube to a glove box.
▲CRITICAL STEP MOF-303 slowly adsorbs water from the atmosphere at ambient conditions. To examine the elemental composition of the activated MOF-303, the sample should be handled under inert conditions (glove box).
- (iv) Transfer the activated MOF-303 in the tube to a dry and preweighed 4 mL dram vial, and record the sample's mass.
- (v) Seal the vial with Teflon tape, and take the vial out of the glove box.
- (vi) Analyze the C, H, N and S content on a Thermo Fisher Flash Smart Elemental analyzer, and record the detection results of each element.

(F) Collecting TGA data ● Timing 3 h

- (i) Transfer ~10 mg of dried MOF-303 onto a clean platinum pan.
- (ii) On a TA Q500 thermal analysis system, record the TGA curve of the sample between 25 °C and 800 °C by ramping at 5°C/min under dry N₂ flow.

We note that alternative instrumentation (e.g., STA449 F5 Jupiter thermogravimetric analyzer from Netzsch) could be utilized for the TGA in a similar manner.

Troubleshooting

Troubleshooting advice can be found in Table 3.

| Step | Problem | Possible reason | Solution |
|---------------------------|---|---|--|
| 1B(ii), 1C(iv), 1D(ii) | Linker not fully dissolved | The dissolution of the base is not complete; thus, the linker is not fully deprotonated, which limits its solubility | Alternate between stirring and sonicating to completely dissolve the NaOH. If possible, use pearl NaOH instead of pellet NaOH for quicker dissolution; add more water (10–30% of the total volume), and stir for 30 min |
| 1B(ii), 1D(ii) | Obtained solution looks yellow | Impurities in the linker | To every 100 mL linker solution, add 1 g activated carbon and stir for 10 min. Use the 100 circles filter paper to purify the obtained solution by vacuum filtration or gravity filtration |
| 1B(vi), 1C(x) | Yield is lower than expected after the reflux or vessel synthesis | The amount of base added to the solution is too low | Use dry and pure NaOH, and weigh quickly to ensure an accurate molar ratio of 3:1 (NaOH: H ₂ PZDC) in the synthesis |
| 2A(ii), 2A(vii) | Two layers of solids are obtained after centrifugation | The top layer consists of undissolved linker or impurities in the reaction and should be removed by further washing | Use an ethanol:water (70:30) mixture as a washing solvent to wash three additional times. If necessary, disperse the solids in the washing mixture, and leave the suspension at ambient conditions for 1 h |
| 3A(i) | The product is still wet after 2 h at 80 °C | The drying is not complete, and a small amount of water remains in the product | Place the solid in a vacuum oven at 100 °C for 2 h |
| 4A(iii) | Peaks in PXRD have low intensity | During the addition, the actual molar ratio between the aluminum salt and linker deviates from 1:1; after the synthesis, the solid is not fully washed and properly dried. Linker molecule may be trapped in the MOF pores, which leads to apparently reduced crystallinity | Double check the purity and mass of both aluminum chloride and linker during the preparation of the solution; suspend the MOF in ethanol, and repeat the washing procedure in Step 3A or Step 3B two additional times. Keep the product in a vacuum oven at 100 °C for 24 h to completely dry it |
| 4C(vi) | The water isotherm shows substantial hysteresis ('Anticipated results') | The MOF-303 crystals exhibit a large number of defects; the majority of product consists of small particles | Make sure the mole ratio between aluminum chloride and linker is 1:1 during the solution preparation; slow down addition rate and double check that the magnetic stir bar is stirring vigorously during the synthesis |
| 4D(iv) | NMR spectrum shows solvent impurities | MOF is not fully activated and contains ethanol | Keep the solids in a 100 °C oven for 12 h |

Timing

Step 1A: 26 h
A(i–v): 1 h
A(vi–vii): 25 h
Step 1B: 6 h
B(i–iii): 1 h
B(iv): 2 h
B(v–vi): 3 h
Step 1C: 10 h
C(i–v): 1 h
C(vi): 2 h
C(vii–viii): 7 h
Step 1D: 30 min
D(i–v): 20 min
D(vi–vii): 10 min
Step 2A: 30 min
Step 2B: 12 h
B(i–ii): 2 h
B(iii–vi): 5 h
B(vii–viii): 5 h
Step 3A: 3 h
Step 3B: 25 h
Step 4A: 15 min
Step 4B: 12 h
Step 4C: 72 h
Step 4D: 10 min
Step 4E: 8 h
Step 4F: 3 h

Anticipated results

MOF-303 is a white solid. Characteristic PXRD patterns (Fig. 6), a digest-¹H-NMR spectrum (Fig. 7), a TGA profile (Fig. 8), nitrogen sorption isotherms (Fig. 9), water vapor sorption isotherms (Fig. 10 and Fig. 11), SEM micrographs (Fig. 12) and elemental analysis results (Table 4) are shown.

After activation, MOF-303 shows only one singlet peak from the pyrazole dicarboxylate linker at 6.7 ppm in its ¹H digestion NMR (Fig. 7), which indicates the high purity of MOF-303. From the solution-state ¹H NMR spectroscopy, we can see that the washing solvent EtOH is completely removed from activated MOF-303. In addition, the good agreement between the calculated and found elemental compositions of MOF-303 samples (Table 4) indicates that all impurities have been removed and no water or ethanol is left in the activated MOF.

PXRD measurements confirm the crystallinity of MOF-303 (Fig. 6).

The TGA confirms the stability of MOF-303 at up to 400 °C and further indicates that the solvent molecules (water and ethanol) can be fully removed upon heating to 120 °C (Fig. 8), which informs our choice for the activation temperature before elemental analysis, as well as before nitrogen and water sorption analysis.

The permanent porosity of MOF-303 samples synthesized with four different methods was examined using nitrogen sorption analysis (Fig. 9). The results demonstrate that all MOF-303 samples have comparable BET surface areas that are >1,300 m²/g.

Finally, we analyze the water uptake properties of these samples. The water vapor sorption isotherms at 25 °C of all MOF-303 samples show a consistent S-shaped profile with a water uptake capacity of 39 wt% at 20% RH and an inflection point at ~12% RH (Fig. 10). Deviations between the water sorption isotherm profiles can be observed for the vessel and microwave methods, which exhibit a steep uptake at high RH ($P/P_{\text{sat}} > 0.8$). This phenomenon can be explained by interparticle condensation (i.e., water vapor condensation between the MOF crystals and not in the MOF pores). This is usually associated with the aggregation of very small crystals, which results in the formation of small interparticle cavities that drive water vapor condensation at a RH <100%. Additionally, a small degree of hysteresis can be observed between the adsorption and desorption curves (i.e., deviation of

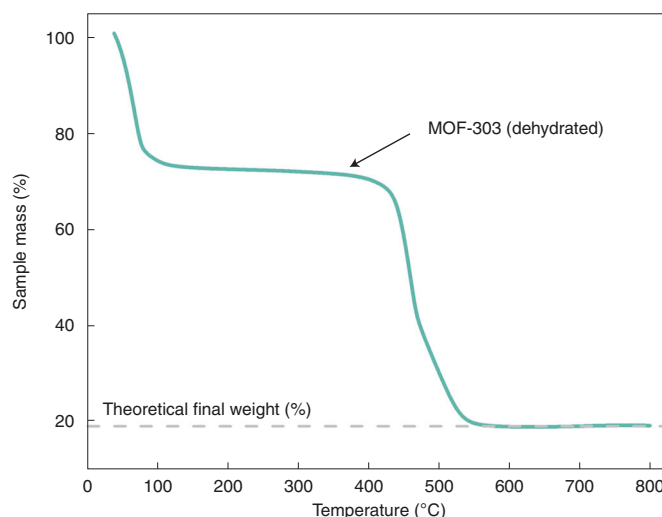


Fig. 8 | TGA profile of MOF-303 synthesized by the vessel method measured under N_2 flow. The first step represents the loss of washing solvents (H_2O and EtOH), and the second step represents the decomposition of the MOF.

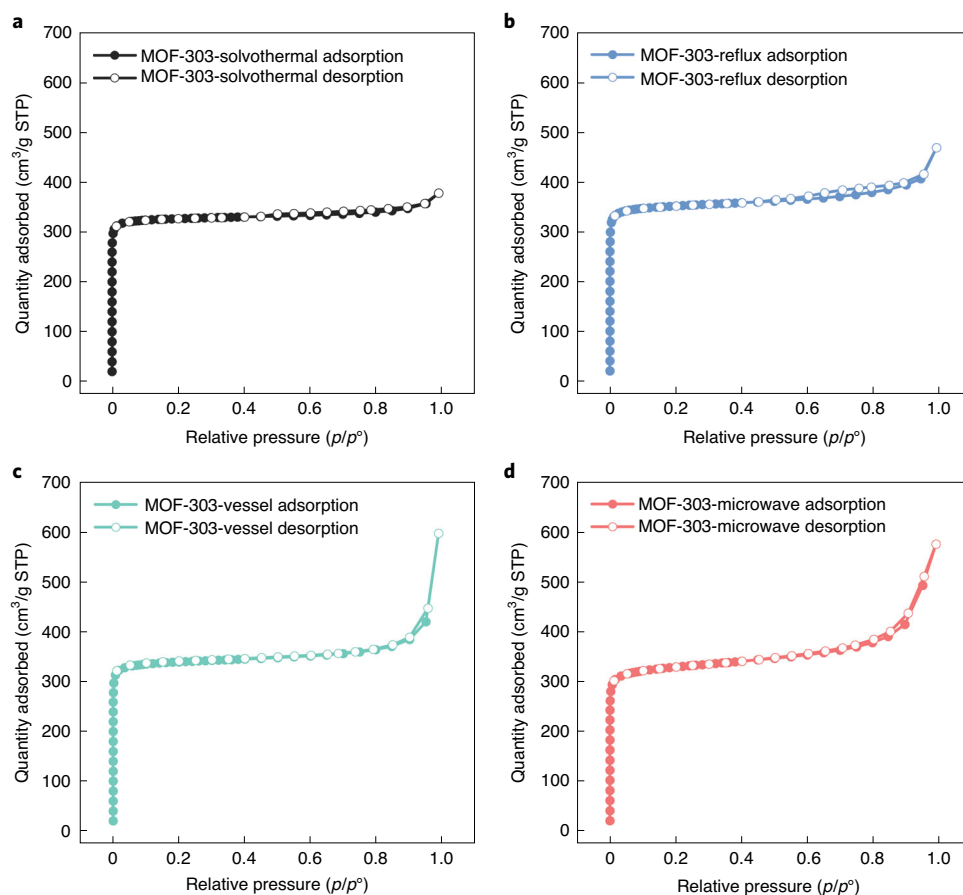


Fig. 9 | N_2 sorption isotherms of MOF-303 samples measured at 77 K. **a**, Solvothermal method (BET surface area $1,342 \text{ m}^2/\text{g}$). **b**, Reflux method (BET surface area $1,384 \text{ m}^2/\text{g}$). **c**, Vessel method (BET surface area $1,380 \text{ m}^2/\text{g}$). **d**, Microwave method (BET surface area $1,307 \text{ m}^2/\text{g}$) measured at 77 K. p , nitrogen pressure; $p^\circ = 1 \text{ atm}$; STP, standard temperature and pressure.

the adsorption branch from the desorption branch of the water sorption isotherm), which we ascribe to the presence of a small number of defective sites within the crystal lattice. The degree of hysteresis is greatly influenced by factors such as the ratios between NaOH, H_2PZDC and $AlCl_3$ used in the

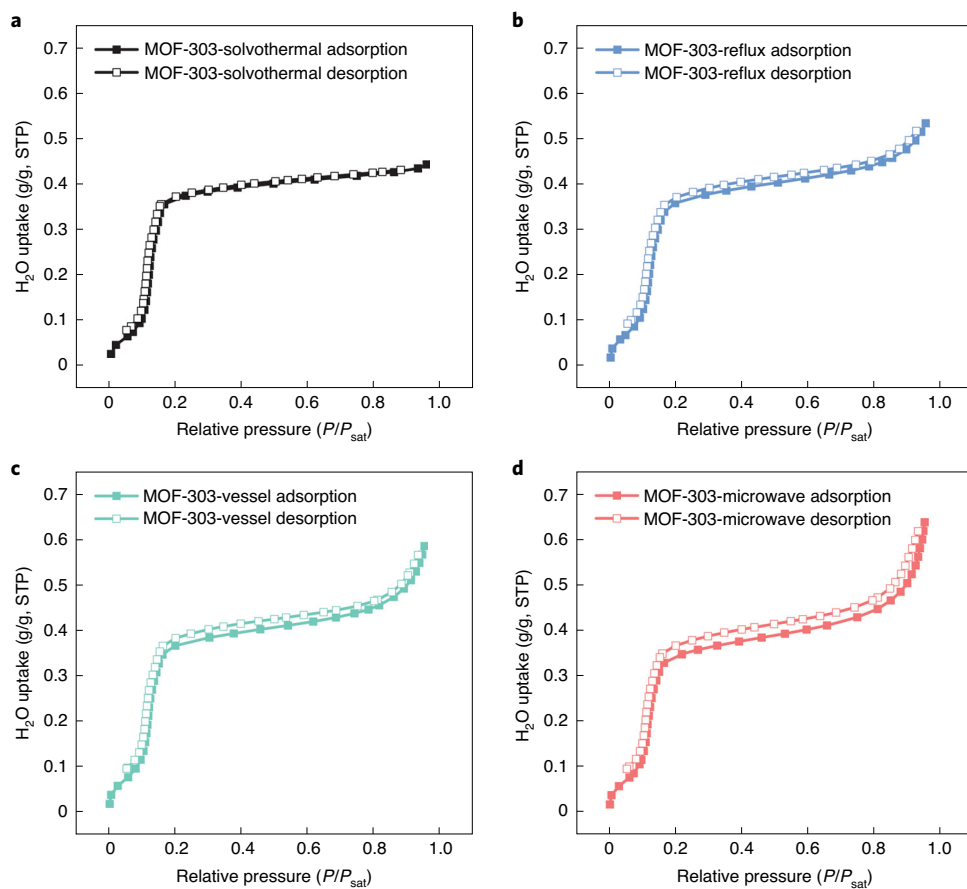


Fig. 10 | Water vapor sorption isotherms of MOF-303 samples measured at 25 °C. **a**, Solvothermal method. **b**, Reflux method. **c**, Vessel method. **d**, Microwave method. P , water vapor pressure; P_{sat} , saturation water vapor pressure.

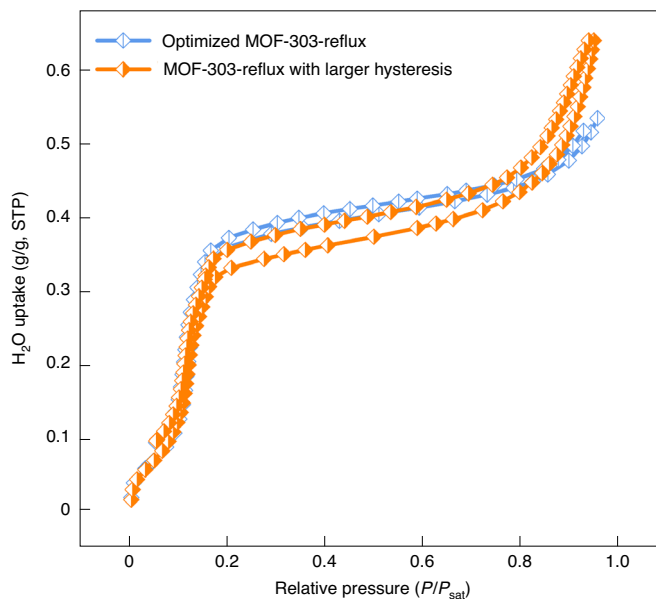


Fig. 11 | Water vapor sorption isotherms of MOF-303-reflux samples with minor hysteresis and substantial hysteresis measured at 25 °C. P , water vapor pressure; P_{sat} , saturation water vapor pressure.

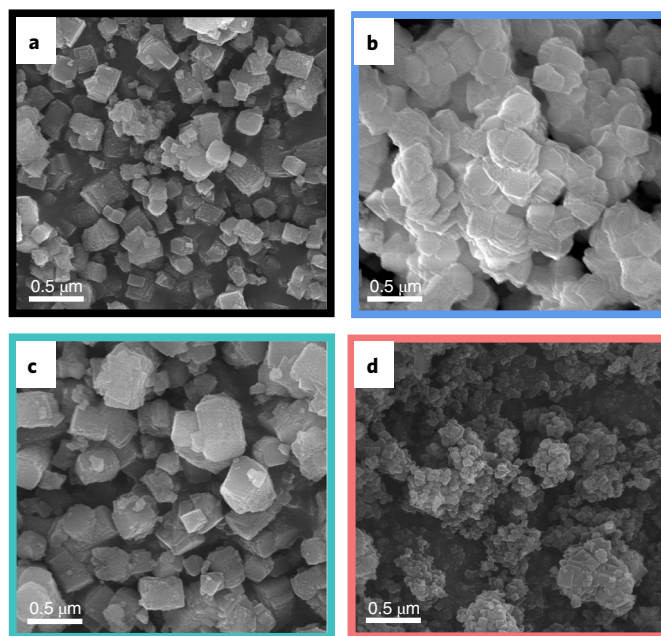


Fig. 12 | SEM images of MOF-303. **a**, Solvothermal method. **b**, Reflux method. **c**, Vessel method. **d**, Microwave method. SEM images were collected on a Hitachi S-5000 high-resolution cold field emission SEM with accelerating voltage of 10.0 kV. The products shown have different particle sizes, which is a result of different reaction concentrations and times. However, their consistent morphology and size distribution leads to similar behavior in their N_2 isotherms and H_2O isotherms.

Table 4 | Elemental analysis of MOF-303 samples synthesized by different methods

| Method | C (%) | H (%) | N (%) | S (%) |
|--------------|-------|-------|-------|-------|
| Calculated | 30.32 | 1.53 | 14.15 | 0 |
| Solvothermal | 29.88 | 1.53 | 13.27 | 0 |
| Reflux | 29.87 | 1.53 | 13.27 | 0 |
| Vessel | 29.77 | 1.58 | 13.40 | 0 |
| Microwave | 29.88 | 1.56 | 13.44 | 0 |

reaction, the $AlCl_3$ solution addition rate and the starting material concentrations used for the MOF synthesis. A larger hysteresis can be observed in the case when the above parameters deviate from the optimal conditions, and a greater deviation between the adsorption and desorption curves can be observed in the water sorption isotherm (Fig. 11).

We use SEM primarily to check if the synthesized products have homogeneous morphology and particle sizes within the same batch/same method (instead of having various sizes of particles ranging from 100 nm to 10 μm). Figure 12 shows that all four methods generate cubic-shape particles, and for the same method the variation in particle size is limited (for 12a: 100–500 nm, 12b: 300–500 nm, 12c: 400–900 nm, 12d: 50–200 nm, all within the nanoscale). They all demonstrate very similar water uptake at low RH. Figure 12d shows a more obvious ‘aggregation’ and smaller particle size, and it is the main reason that the adsorption curve shown in Fig. 10d does not perfectly match with the desorption curve at high RH. The overall performance at low RH is not affected by this slight difference.

Data availability

The raw data for water vapor sorption and nitrogen sorption are available at <https://doi.org/10.6084/m9.figshare.19859002.v3>.

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Author contributions

Z. Zheng, H.L.N., N.H. and O.M.Y. designed the experiments; Z. Zheng and N.H. performed the syntheses of MOF-303; Z. Zheng and H.L.N. designed the purification of MOF-303 and analyzed the collected data with guidance from O.M.Y.; Z. Zheng, H.L.N., K.K.-Y.L. and Z. Zhou performed the purification of kilogram-scale MOF-303. N.H. collected the water vapor isotherms of MOF-303 samples and interpreted the data; T.M. recorded SEM images for MOF-303 samples. All authors wrote the manuscript.

Competing interests

O.M.Y. is co-founder of Water Harvesting Inc., aiming at commercializing related technologies.

Additional information

Correspondence and requests for materials should be addressed to Omar M. Yaghi.

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