

Seed-Mediated Synthesis of Metal–Organic Frameworks

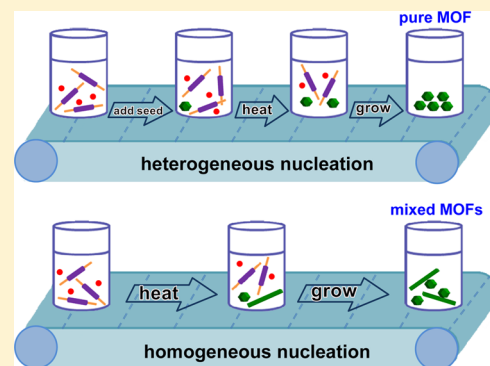
Hai-Qun Xu,[†] Kecheng Wang,[‡] Meili Ding,[†] Dawei Feng,[‡] Hai-Long Jiang,^{*,†} and Hong-Cai Zhou^{*,‡}

[†]Hefei National Laboratory for Physical Sciences at the Microscale, CAS Key Laboratory of Soft Matter Chemistry, Collaborative Innovation Center of Suzhou Nano Science and Technology, Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, PR China

[‡]Department of Chemistry, Texas A&M University, College Station, Texas 77843, United States

S Supporting Information

ABSTRACT: The synthesis of phase-pure metal–organic frameworks (MOFs) is of prime importance but remains a significant challenge because of the flexible and diversified coordination modes between metal ions and organic linkers. In this work, we report the synthesis of phase-pure MOFs via a facile seed-mediated approach. For several “accompanying” pairs of Zr–porphyrinic MOFs that are prone to yield mixtures, by fixing all reaction parameters except introducing seed crystals, MOFs in phase-pure forms have been obtained because the stage of MOF nucleation, which generates mixed nuclei, is bypassed. In addition, phase-pure MOF isomers with distinct pore structures have also been prepared through such an approach, revealing its versatility. To the best of our knowledge, this is an initial report on seed-assisted synthesis of phase-pure MOFs.



INTRODUCTION

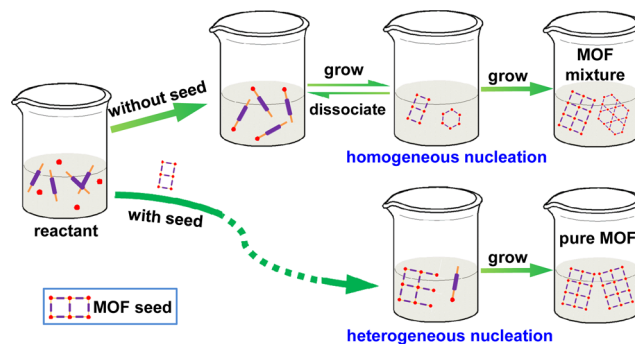
As a relatively new class of porous materials, metal–organic frameworks (MOFs), also known as porous coordination polymers, have attracted growing interest in recent two decades because of their crystalline nature, tunable structures/properties, and potential applications as functional materials in many fields.^{1–5} MOFs are constructed from metal ions/clusters and multitopic organic struts linked through coordination bonds. Given the flexible and diversified coordination modes, the combination of the same organic ligand and metal unit may afford a variety of MOFs with distinct structures under similar or even identical reaction conditions.⁶ However, this also causes an undesired but common issue in MOF synthesis: Two or more phases are formed in a one-pot reaction, and the separation of them is difficult, which severely hampers the application of the obtained MOFs because even structurally similar MOFs have enormously different properties.^{6b,7} To address such an issue, Hupp, Farha, and co-workers have reported a solvent-assisted separation of mixed MOFs on the basis of their density difference;^{8a} metal–organic polyhedra (MOPs) can also be separated similarly, which has been demonstrated by Yaghi and co-workers.^{8b} Despite its effectiveness, the method is limited because the density difference has to be distinct and the separating parent solvent CH₂BrCl is toxic. Therefore, it is imperative to develop a general and eco-friendly approach to facilitate the separation of mixed MOFs that are prone to form in a one-pot reaction.

To obtain phase-pure MOFs, which can be assessed by powder X-ray diffraction (PXRD), it is necessary to review the mechanism of crystal growth. In the case of a homogeneous nucleation, clusters that are smaller than critical sizes are

formed first in the system in a nearly supersaturated solution. Subsequently, different clusters may combine or split during the initial growth. These association and dissociation processes reach a dynamic equilibrium, possibly yielding a variety of MOF nuclei. Consequently, this leads to MOFs in mixed phases because nuclei surpassing the critical size will evolve into crystals (Scheme 1, top). The energy required in the nucleation stage gradually increases to a maximum when nucleus of critical size attains and decreases thereafter (Scheme S1a).⁹

In addition to the above homogeneous nucleation, heterogeneous nucleation of MOFs with matched crystal

Scheme 1. Schematic Illustration of the Traditional Process of MOF Crystal Growth (Homogeneous Nucleation) and the Strategy for Seed-Mediated Growth of Phase-Pure MOFs (Heterogeneous Nucleation)



Received: February 7, 2016

Published: March 25, 2016

lattices also occurs when foreign particles/components are present (Scheme 1, bottom), which has been well-established for large crystal growth by a seeded solution method.^{9,10} Moreover, the heterogeneous process requires much lower driving force than does the homogeneous one. (See Supporting Information, section 1) In this sense, the introduction of seed crystals of the particular MOF into the reaction system would enable the growth of the particular MOF, which is kinetically favored, because the nucleation stage is bypassed. Meanwhile, once the MOF growth starts, the precursor concentration gradually decreases, making the nucleation and crystal growth of undesired phases more difficult, which results in the formation of pure target MOF product only (Supporting Information, section 2).

With the above considerations in mind, we explored seed-mediated synthesis of phase-pure MOFs. Recently, Zr-carboxylate MOFs have been extensively studied because of their ultrahigh stability.^{11,12} Particularly, Zr-MOFs based on tetrakis(4-carboxyphenyl)porphyrin (TCPP) are highly sought after because of the built-in multifunctionality. We and others have reported diverse Zr-TCPP MOFs, exhibiting exceptional stability and various functionalities recently.¹² These Zr-MOFs are all obtained from ZrCl₄ and TCPP ligand under similar reaction conditions. Consequently, the preparation of these MOFs in their phase-pure forms remains a formidable challenge. Moreover, the “accompanying” MOF pairs, which associate with each other throughout the synthesis procedure, are difficult to separate into phase-pure forms.^{12a–e} Typical examples of these accompanying MOF pairs are PCN-222(Ni) and PCN-224(Ni), PCN-222 and PCN-225, as well as PCN-222(Zn) and PCN-225(Zn). (The metal in the parentheses represents the metal ion residing in the TCPP center.) These Zr-MOF pairs possess similar density and thus are hardly separated via the aforementioned solvent-induced method.⁸ Fortunately, all three pairs of MOFs (Figure 1a–c) can be

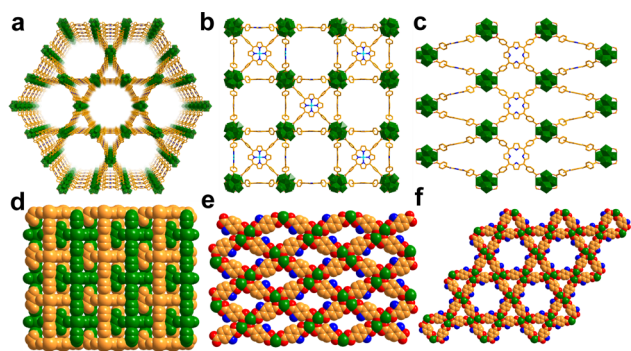


Figure 1. View of the structures of (a) PCN-222, (b) PCN-224(Ni), and (c) PCN-225 in a ball–stick fashion. The ZrO₆ octahedra are shaded in green. View of the structures of (d) nonCd, (e) microCd, and (f) mesoCd in a space-filling fashion, highlighting their different channel sizes.

prepared in phase-pure forms via a seed-mediated approach reliably, which would otherwise be difficult or impossible. In addition, a Cd-MOF triad, three MOF isomers with distinct pore structures (Figure 1d–f),¹³ usually obtained with impurities or accompanying one another, have also been prepared in their phase-pure forms via such a strategy, revealing its versatility. To the best of our knowledge, this is an initial report on the synthesis of phase-pure MOFs with a seed-assisted strategy.

MATERIALS AND METHODS

Materials. Methyl 4-formylbenzoate, zirconium(IV) chloride, nickel(II) chloride hexahydrate, zinc(II) chloride, cadmium(II) nitrate tetrahydrate, 4,4'-bipy, and pyrrole were purchased from Energy Chemical. Propionic acid was from Aladdin Industrial Inc. 2-aminoterephthalic acid (H₂APTA) was from Sigma-Aldrich. N,N-Dimethylformamide (DMF), N,N-diethylformamide (DEF) was from Alfa Aesar. Acetic acid, and benzoic acid were purchased from Sinopharm Chemical Reagent Co., Ltd. Tetrakis(4-carboxyphenyl)porphyrin (H₂TCPP) and [5,10,15,20-tetrakis(4-carboxyphenyl)porphyrinato]-Ni(II) (Ni-TCPP) ligands were synthesized according to previous reports (Supporting Information, section 3).^{12b} All commercial chemicals were used without further purification.

Instrumentation. Powder X-ray diffraction patterns (PXRD) were collected on a Japan Rigaku SmartLab rotation anode X-ray diffractometer, a Holland X'Pert PRO fixed anode X-ray diffractometer, a BRUKER D8-Focus Bragg–Brentano X-ray powder diffractometer, a Rigaku MiniFlex600 X-ray Diffractometer equipped with graphite monochromatized Cu K α radiation ($\lambda = 1.54 \text{ \AA}$). Field-emission scanning electron microscopy (FE-SEM) was carried out with a field-emission scanning electron microanalyzer (Zeiss Supra 40 scanning electron microscope at an acceleration voltage of 5 kV). Thermogravimetric analysis (TGA) was conducted on a SHIMADZU DTG-60H thermogravimetric analyzer. N₂ adsorption–desorption isotherms were measured using a Micromeritics ASAP 2420 or ASAP 2020 system.

Synthesis of MOFs via Different Recipes. *Recipe a.* A mixture of ZrCl₄ (10 mg), Ni-TCPP (10 mg), and benzoic acid (350 mg) was ultrasonically dissolved in 1.75 mL of DMF and 0.25 mL of DEF in a 4 mL vial. The mixture was heated at 120 °C in an oven for 24 h. After cooling to room temperature, the products were harvested by filtration, washing, and drying.

Recipe b. A mixture of ZrCl₄ (100 mg), H₂TCPP (40 mg), benzoic acid (2700 mg), and 20 drops of acetic acid was ultrasonically dissolved in 8 mL of DEF in a 20 mL vial. The mixture was heated at 120 °C in an oven for 12 h. After cooling to room temperature, the products were harvested by filtration, washing, and drying.

Recipe c. A mixture of ZrCl₄ (70 mg), H₂TCPP (50 mg), and benzoic acid (2700 mg) was ultrasonically dissolved in 8 mL of DEF in a 20 mL vial. The mixture was heated at 120 °C in an oven for 12 h. After cooling to room temperature, the products were harvested by filtration, washing, and drying.

Recipe d. A mixture of ZrCl₄ (70 mg), H₂TCPP (50 mg), ZnCl₂ (50 mg), and benzoic acid (2700 mg) was ultrasonically dissolved in 8 mL of DEF in a 20 mL vial. The mixture was heated at 120 °C in an oven for 12 h. After cooling to room temperature, the products were harvested by filtration, washing, and drying.

Recipe e. A mixture of ZrCl₄ (60 mg), H₂TCPP (50 mg), ZnCl₂ (50 mg), and benzoic acid (2500 mg) was ultrasonically dissolved in 9 mL of DEF in a 20 mL vial. The mixture was heated at 120 °C in an oven for 12 h. After cooling to room temperature, the products were harvested by filtration, washing, and drying.

Recipe f. A mixture of Cd(NO₃)₂·4H₂O (108 mg), H₂APTA (47 mg), and BPY (41 mg) was ultrasonically dissolved in 6.5 mL of DMF in a 21 mL Teflon-lined bomb. The mixture was heated at 160 °C in an oven for 72 h. After cooling to room temperature, the products were harvested by filtration, washing, and drying.

Recipe g. A mixture of Cd(NO₃)₂·4H₂O (108 mg), H₂APTA (47 mg), and BPY (41 mg) was ultrasonically dissolved in 4.4 mL of DMF in a 21 mL Teflon-lined bomb. The mixture was heated at 105 °C in an oven for 24 h. After cooling naturally, the crystals were obtained. Because of the air sensitivity of microCd, the PXRD studies in air should be performed with a little mother liquid.

Recipe h. A mixture of Cd(NO₃)₂·4H₂O (108 mg), H₂APTA (47 mg), and BPY (41 mg) was ultrasonically dissolved in 6 mL of DMF in a 21 mL Teflon-lined bomb. The mixture was heated at 105 °C in an oven for 10 h. Because of the air sensitivity of mesoCd, the PXRD studies should be performed with a little mother liquid once it was taken out from Teflon-lined reactor in air.

RESULTS AND DISCUSSION

PCN-224(Ni) and PCN-222(Ni) were usually prepared as an accompanying pair (Table 1, entry 1). Phase-pure PCN-

Table 1. Summary of the Probability of Resultant Phase-Pure MOFs Obtained in the Absence or Presence of Corresponding Exogenous MOF Seeds in the Reaction Mixture

entry	recipe	seed	product ^a
1		no seed	~0% pure phase
2	a	PCN-222(Ni)	100% PCN-222(Ni)
3		PCN-224(Ni)	100% PCN-224(Ni)
4		no seed	10% PCN-222 with poor crystallinity, 5% PCN-225
5	b	PCN-222	100% PCN-222
6		PCN-225	100% PCN-225
7		no seed	70% PCN-222 with poor crystallinity, 0% PCN-225
8	c	PCN-222	100% PCN-222
9		PCN-225	100% PCN-225
10		no seed	10% PCN-222(Zn), 20% PCN-225(Zn)
11	d	PCN-222(Zn)	100% PCN-222(Zn)
12		PCN-225(Zn)	100% PCN-225(Zn)
13		no seed	0% PCN-222(Zn), 30% PCN-225(Zn)
14	e	PCN-222(Zn)	100% PCN-222(Zn)
15		PCN-225(Zn)	100% PCN-225(Zn)
16	f	no seed	40% nonCd
17		nonCd	100% nonCd
18		no seed	30% microCd
19	g	microCd	100% microCd
20		no seed	30% mesoCd
21	h	mesoCd	100% mesoCd

^aThe probability indicated here is based on our limited experimental attempts (over 10 trials for each recipe).

222(Ni) and PCN-224(Ni) microcrystals in rod and cube shape, respectively, both of which can be obtained on the basis of the previous reports (Supporting Information, section 4),^{12b,e} in low probabilities, were added to a reaction mixture of ZrCl₄, Ni-TCPP, and benzoic acid in a mixed solvent of DMF and DEF, respectively, which was heated at 120 °C for 24 h (recipe a). Although recipe a hardly affords phase-pure MOF in the absence of particular MOF seeds, remarkably, the respective phase-pure MOF in a high yield can be harvested with almost 100% probability when PCN-222(Ni) or PCN-224(Ni) seeds were introduced (Table 1, entries 2 and 3). PXRD studies demonstrated the effectiveness of seed-induced phase separation (Figures 2a and S1). It should be noted that, although such seed-mediated growth of MOF crystals does not necessarily lead to large single crystals in our experiments, the crystallinity of the resultant powder is high as evidenced by the sharp peaks in PXRD patterns (Figure 2a).

Similarly, lots of explorations demonstrate that the production of pure PCN-225 is very challenging. The optimized reaction conditions (recipe b) of heating a mixture of ZrCl₄, H₂TCPP, benzoic acid, and acetic acid in DEF for 12 h only gave ~5% probability of success (Table 1, entry 4), which was calculated from a total of 20 attempts that gave 1 case of pure PCN-225, 2 cases of pure PCN-222, and 17 cases of mixed phases. Amazingly, phase-pure PCN-225 or PCN-222 can be prepared every single time, corresponding to a probability of 100%, by adding their respective seeds (in

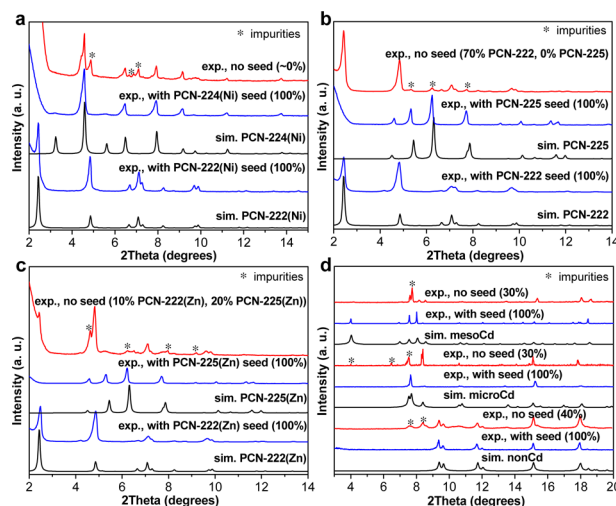


Figure 2. PXRD patterns for (a) PCN-222(Ni) and PCN-224(Ni), (b) PCN-222 and PCN-225, (c) PCN-222(Zn) and PCN-225(Zn), as well as (d) nonCd, microCd, and mesoCd obtained in the absence or presence of respective seeds. The asterisks indicate the peaks assigned to impurities.

polyhedron and rod shape, respectively), both of which were provided via recipe b, even in low probabilities. Only a visible (to the naked eye) amount of seeds were introduced to the reaction mixture, which was followed by exactly the same reaction conditions without changing any other parameters (Table 1, entries 5 and 6; Figure S2).

When the reaction conditions were changed to recipe c in the absence of exogenous seeds, 70% of the attempts led to phase-pure PCN-222, and the rest yielded mixtures; no phase-pure PCN-225 can be obtained (Table 1, entry 7). In contrast, both phase-pure PCN-222 and PCN-225 can be readily produced every time, corresponding to a probability of 100%, under almost identical conditions except that their respective seeds (obtained via recipe b) were introduced into the reaction mixture (Table 1, entries 8 and 9; Figures 2b and S3).

The case is even more exciting for the subsequent accompanying pair of PCN-222(Zn) and PCN-225(Zn). In the optimized recipe d for the synthesis of PCN-222(Zn) in the absence of seeds, only 10% of the cases are successful (Table 1, entry 10). Under identical conditions, however, upon the addition of target seeds (in rod and polyhedron shape, respectively for PCN-222(Zn) and PCN-225(Zn)) obtained via recipe d, both phase-pure PCN-222(Zn) and PCN-225(Zn) can be prepared in every case (Table 1, entries 11 and 12; Figures 2c and S4). Conversely, recipe e produces pure PCN-225(Zn) in 30% of the cases, whereas all other attempts afforded mixture in the absence of seeds (Table 1, entry 13). Both MOFs in their phase-pure forms can be obtained with the introduction of their respective seeds (produced via recipe d) under almost identical reaction conditions (Table 1, entries 14 and 15; Figure S5) other than seed addition.

To gain additional evidence for phase-pure MOF synthesis via the seed-mediated approach, scanning electron microscope (SEM) images of the products were taken. As displayed in Figures 3, S6 and S7, mixed MOFs with different shapes were generated in the absence of seeds or presence of mixed MOF seeds. In contrast, phase-pure MOFs can be obtained under the same conditions by the introduction of MOF seeds of a single phase.

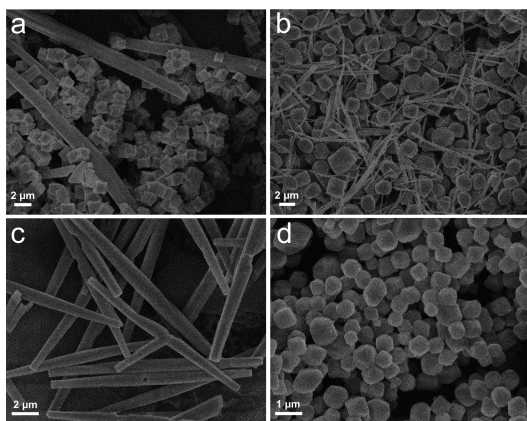


Figure 3. SEM images for the products obtained via recipe *e* (a) in the absence of seeds, (b) in the presence of mixed PCN-222(Zn) and -225(Zn) seeds, (c) in the presence of PCN-222(Zn) seeds, and (d) in the presence of PCN-225(Zn) seeds.

These compelling results suggest that despite the change of reaction parameters in a certain range, the introduction of phase-pure seeds (Figure S8) into the reaction mixture constitutes the only prerequisite for seed-mediated synthesis of phase-pure MOFs. This implies that once a small amount of pure MOF is obtained, even if it usually accompanies undesired phases under its synthetic conditions, its phase-pure form can be obtained reliably through this simple strategy. In addition to the cogent PXRD and SEM evidence, both thermogravimetric analysis (TGA) and gas sorption data for the representative accompanying pair of PCN-222(Zn) and PCN-225(Zn) support such a statement (Figures S9 and S10).

All the experimental data revealed that the phase-pure MOF products generated via such a seed-mediated approach were identical to those obtained through traditional solvothermal synthetic routes (Figures 2c, S4, S5, S9, and S10) despite the stark difference in product purity. Moreover, the exogenous seeds introduced before the commencement of crystallization enable the crystal growth process to bypass the most energy-intensive step, the dynamic dissociation-growth equilibrium of crystal clusters (Supporting Information, section 1). Therefore, the seed-mediated synthesis offers a more efficient and faster alternative than the prior approaches. Preliminary kinetic studies provided convincing evidence for such an argument. A reaction via the seed-mediated approach afforded the anticipated MOF product within 6 h, whereas in a control experiment of traditional solvothermal synthesis, the reaction mixture remains clear after 6 h (Figure 4).

The foregoing results have unambiguously illustrated that the seed-mediated approach is powerful for the preparation of phase-pure Zr-TCPP MOFs. To demonstrate the versatility of this strategy, we also applied it in the separation of a triad of accompanying Cd-MOFs. These three MOF isomers, having distinct pore structures, are usually obtained with impurities or accompanying one another. These Cd-MOFs are nonporous, microporous, and mesoporous, respectively, denoted as nonCd, microCd, and mesoCd. They are based on the same Cd₂ building unit as well as 4,4'-bipy (BPY) and 2-amino-terephthalic acid (H₂APTA) ligands (Figure 1d–f).¹³ In particular, they are MOF isomers with highly correlated structures: Unraveling of twofold interpenetrated nonCd leads to noninterpenetrated microCd; microCd and mesoCd can be reversibly transformed upon the application of external

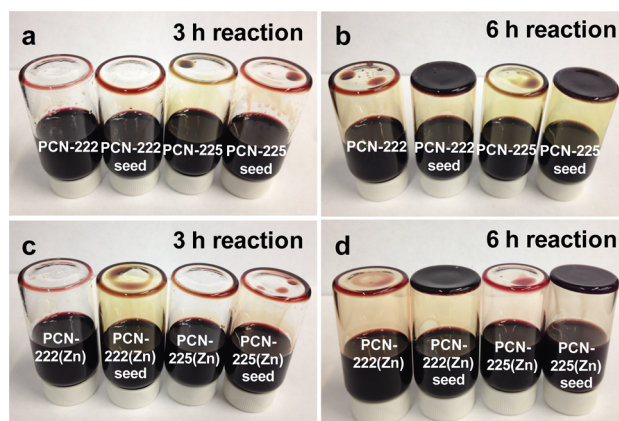


Figure 4. Reaction speed investigation based on different synthetic methods. (a and b) Synthesis of PCN-222 and PCN-225 via traditional synthesis (marked as PCN-222 and PCN-225) or seed-mediated approach (marked as PCN-222 seed and PCN-225 seed). (c and d) Synthesis of PCN-222(Zn) and PCN-225(Zn) via traditional synthesis (marked as PCN-222(Zn) and PCN-225(Zn)) or seed-mediated approach (marked as PCN-222(Zn) seed and PCN-225(Zn) seed).

stimuli. In this context, the overlapping of the synthetic parameters and the difficulty to obtain these Cd-MOFs in phase-pure forms are obvious. Tremendous effort (~1000 vials) was devoted to show that the same amounts of metal precursor and ligands with subtle alteration of solvent amount or reaction temperature can provide their respective pure phases, but with limited success (Table 1, entries 16, 18, and 20). Similarly, when the respective seeds (obtained via recipes *f–h*, respectively; see Supporting Information, section 4) of these Cd-MOFs were introduced, all three MOFs in phase-pure forms were obtained with ~100% of probability. The PXRD patterns of these phase-pure MOFs closely matched the simulated ones (Figures 2d and S11–13), once again demonstrating the general success of this seed-mediated synthetic strategy. It is well-known that the interpenetrated and noninterpenetrated pair of MOFs are generally concomitant and difficult to separate.^{6–8} Meanwhile, the separation of them is of vital importance because their functions are significantly different.^{6,7} The current seed-mediated approach offers an effective solution to meet this challenge. The successful separation of the three Cd-MOF isomers paves the way to the preparation of pure MOF isomers in the future.

CONCLUSIONS

The effective separation of diverse MOF mixtures and synthesis of phase-pure MOFs have been successfully achieved via a facile seed-mediated approach. Introducing seeds of a targeted MOF in the reaction system brings on significant purity improvement in the resultant MOF product in various synthesis systems. The strategy is very straightforward and worth trying in phase-pure synthesis of a variety of MOFs. The only prerequisite for this approach is that the target MOF seeds even if in a minute amount should be introduced. Given the extensive studies on broad applications of MOFs, the production of phase-pure MOFs in a large scale is of fundamental importance. It is thus believed that the current synthetic strategy can greatly benefit the MOF research field and may even be extendable to the synthesis of other crystalline materials.

■ ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b01414.

Full experimental details and characterization data. (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*jianglab@ustc.edu.cn

*zhou@chem.tamu.edu

Author Contributions

H.-Q. X. and K. W. contributed equally to this work.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The Zr-MOF work was partially supported by the Center for Gas Separations Relevant to Clean Energy Technologies, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-SC0001015. H.L.J. gratefully acknowledges the support of NSFC (21371162, 51301159, and 21521001), the 973 Program (2014CB931803), the Recruitment Program of Global Experts, and the Fundamental Research Funds for the Central Universities (WK2060190026, WK2060190065).

■ REFERENCES

- (1) (a) Long, J. R.; Yaghi, O. M. *Chem. Soc. Rev.* **2009**, *38*, 1213. (b) Zhou, H.-C.; Long, J. R.; Yaghi, O. M. *Chem. Rev.* **2012**, *112*, 673. (c) Furukawa, H.; Cordova, K. E.; O'Keeffe, M.; Yaghi, O. M. *Science* **2013**, *341*, 974. (d) Cook, T. R.; Zheng, Y.-R.; Stang, P. J. *Chem. Rev.* **2013**, *113*, 734. (e) Zhou, H.-C.; Kitagawa, S. *Chem. Soc. Rev.* **2014**, *43*, 5415.
- (2) (a) Liu, J.; Thallapally, P. K.; McGrail, B. P.; Brown, D. R.; Liu, J. *Chem. Soc. Rev.* **2012**, *41*, 2308. (b) Sumida, K.; Rogow, D. L.; Mason, J. A.; McDonald, T. M.; Bloch, E. D.; Herm, Z. R.; Bae, T.-H.; Long, J. R. *Chem. Rev.* **2012**, *112*, 724. (c) Suh, M. P.; Park, H. J.; Prasad, T. K.; Lim, D.-W. *Chem. Rev.* **2012**, *112*, 782. (d) Rodenas, T.; Luz, I.; Prieto, G.; Seoane, B.; Miro, H.; Corma, A.; Kapteijn, F.; Llabrés i Xamena, F. X.; Gascon, J. *Nat. Mater.* **2015**, *14*, 48. (e) Li, J.-R.; Sculley, J.; Zhou, H.-C. *Chem. Rev.* **2012**, *112*, 869. (f) Nugent, P.; Belmabkhout, Y.; Burd, S. D.; Cairns, A. J.; Luebke, R.; Forrest, K.; Pham, T.; Ma, S.; Space, B.; Wojtas, L.; Eddaoudi, M.; Zaworotko, M. J. *Nature* **2013**, *495*, 80.
- (3) (a) Seo, J. S.; Whang, D.; Lee, H.; Jun, S. I.; Oh, J.; Jeon, Y. J.; Kim, K. *Nature* **2000**, *404*, 982. (b) Farrusseng, D.; Aguado, S.; Pinel, C. *Angew. Chem., Int. Ed.* **2009**, *48*, 7502. (c) Jiang, H.-L.; Xu, Q. *Chem. Commun.* **2011**, *47*, 3351. (d) Kreno, L. E.; Leong, K.; Farha, O. K.; Allendorf, M.; Van Duyne, R. P.; Hupp, J. T. *Chem. Rev.* **2012**, *112*, 1105. (e) Zhang, T.; Lin, W. *Chem. Soc. Rev.* **2014**, *43*, 5982. (f) Liu, J.; Chen, L.; Cui, H.; Zhang, J.; Zhang, L.; Su, C.-Y. *Chem. Soc. Rev.* **2014**, *43*, 6011. (g) Li, X.; Guo, Z.; Xiao, C.; Goh, T. W.; Tesfagaber, D.; Huang, W. Y. *ACS Catal.* **2014**, *4*, 3490. (h) Lin, Q.; Bu, X.; Kong, A.; Mao, C.; Zhao, X.; Bu, F.; Feng, P. *J. Am. Chem. Soc.* **2015**, *137*, 2235. (i) Liao, P.-Q.; Zhang, W.-X.; Zhang, J.-P.; Chen, X.-M. *Nat. Commun.* **2015**, *6*, 8697.
- (4) (a) Chen, B.; Xiang, S.; Qian, G. *Acc. Chem. Res.* **2010**, *43*, 1115. (b) Li, C.-P.; Du, M. *Chem. Commun.* **2011**, *47*, 5958. (c) Yan, Y.; Suyetin, M.; Bichoutskaia, E.; Blake, A. J.; Allan, D. R.; Barnett, S. A.; Schroder, M. *Chem. Sci.* **2013**, *4*, 1731. (d) Hu, Z.; Deibert, B. J.; Li, J. *Chem. Soc. Rev.* **2014**, *43*, 5815. (e) Zhang, H.-X.; Liu, M.; Wen, T.; Zhang, J. *Coord. Chem. Rev.* **2016**, *307*, 255.
- (5) (a) An, J.; Geib, S. J.; Rosi, N. L. *J. Am. Chem. Soc.* **2009**, *131*, 8376. (b) Kitagawa, H. *Nat. Chem.* **2009**, *1*, 689. (c) Klein, N.; Senkovska, I.; Gedrich, K.; Stoeck, U.; Henschel, A.; Mueller, U.; Kaskel, S. *Angew. Chem., Int. Ed.* **2009**, *48*, 9954. (d) Horcajada, P.; Gref, R.; Baati, T.; Allan, P. K.; Maurin, G.; Couvreur, P.; Férey, G.; Morris, R. E.; Serre, C. *Chem. Rev.* **2012**, *112*, 1232. (e) Brozek, C. K.; Dincă, M. *Chem. Sci.* **2012**, *3*, 2110. (f) Mallick, A.; Garai, B.; Díaz, D. D.; Banerjee, R. *Angew. Chem., Int. Ed.* **2013**, *52*, 13755. (g) Fang, Z.; Bueken, B.; De Vos, D. E.; Fischer, R. A. *Angew. Chem., Int. Ed.* **2015**, *54*, 7234. (h) Ramaswamy, P.; Wong, N. E.; Shimizu, G. K. H. *Chem. Soc. Rev.* **2014**, *43*, 5913. (i) Denny, M. S.; Cohen, S. M. *Angew. Chem., Int. Ed.* **2015**, *54*, 9029.
- (6) (a) Zheng, B.; Dong, H.; Bai, J.; Li, Y.; Li, S.; Scheer, M. J. *Am. Chem. Soc.* **2008**, *130*, 7778. (b) Jiang, H.-L.; Makal, T. A.; Zhou, H.-C. *Coord. Chem. Rev.* **2013**, *257*, 2232.
- (7) Ma, S.; Sun, D.; Ambrogio, M.; Fillingner, J. A.; Parkin, S.; Zhou, H.-C. *J. Am. Chem. Soc.* **2007**, *129*, 1858.
- (8) (a) Farha, O. K.; Mulfort, K. L.; Thorsness, A. M.; Hupp, J. T. *J. Am. Chem. Soc.* **2008**, *130*, 8598. (b) Sudik, A. C.; Millward, A. R.; Ockwig, N. W.; Côté, A. P.; Kim, J.; Yaghi, O. M. *J. Am. Chem. Soc.* **2005**, *127*, 7110.
- (9) Sunagawa, I. *Crystals Growth, Morphology and Perfection*; Cambridge University Press: Cambridge, U.K., 2005; pp 20–59.
- (10) (a) Koh, K.; Wong-Foy, A. G.; Matzger, A. J. *Chem. Commun.* **2009**, 6162. (b) Hirai, K.; Furukawa, S.; Kondo, M.; Uehara, H.; Sakata, O.; Kitagawa, S. *Angew. Chem., Int. Ed.* **2011**, *50*, 8057. (c) Liu, L.; Konstas, K.; Hill, M. R.; Telfer, S. G. *J. Am. Chem. Soc.* **2013**, *135*, 17731.
- (11) (a) Cavka, J. H.; Jakobsen, S.; Olsbye, U.; Guillou, N.; Lamberti, C.; Bordiga, S.; Lillerud, K. P. *J. Am. Chem. Soc.* **2008**, *130*, 13850. (b) Schaate, A.; Roy, P.; Preuße, T.; Lohmeier, S. J.; Godt, A.; Behrens, P. *Chem. - Eur. J.* **2011**, *17*, 9320. (c) Mondloch, J. E.; Bury, W.; Fairen-Jimenez, D.; Kwon, S.; DeMarco, E. J.; Weston, M. H.; Sarjeant, A. A.; Nguyen, S. T.; Stair, P. C.; Snurr, R. Q.; Farha, O. K.; Hupp, J. T. *J. Am. Chem. Soc.* **2013**, *135*, 10294. (d) Yee, K.-K.; Reimer, N.; Liu, J.; Cheng, S.-Y.; Yiu, S.-M.; Weber, J.; Stock, N.; Xu, Z. *J. Am. Chem. Soc.* **2013**, *135*, 7795. (e) Feng, D.; Wang, K.; Su, J.; Liu, T.-F.; Park, J.; Wei, Z.; Bosch, M.; Yakovenko, A.; Zou, X.; Zhou, H.-C. *Angew. Chem., Int. Ed.* **2015**, *54*, 149.
- (12) (a) Morris, W.; Voloskiy, B.; Demir, S.; Gándara, F.; McGrier, P. L.; Furukawa, H.; Cascio, D.; Stoddart, J. F.; Yaghi, O. M. *Inorg. Chem.* **2012**, *51*, 6443. (b) Feng, D.; Gu, Z.-Y.; Li, J.-R.; Jiang, H.-L.; Wei, Z.; Zhou, H.-C. *Angew. Chem., Int. Ed.* **2012**, *51*, 10307. (c) Chen, Y.; Hoang, T.; Ma, S. *Inorg. Chem.* **2012**, *51*, 12600. (d) Jiang, H.-L.; Feng, D.; Wang, K.; Gu, Z.-Y.; Wei, Z.; Chen, Y.-P.; Zhou, H.-C. *J. Am. Chem. Soc.* **2013**, *135*, 13934. (e) Feng, D.; Chung, W.-C.; Wei, Z.; Gu, Z.-Y.; Jiang, H.-L.; Chen, Y.-P.; Darensbourg, D. J.; Zhou, H.-C. *J. Am. Chem. Soc.* **2013**, *135*, 17105. (f) Feng, D.; Jiang, H.-L.; Chen, Y.-P.; Gu, Z.-Y.; Wei, Z.; Zhou, H.-C. *Inorg. Chem.* **2013**, *52*, 12661. (g) Feng, D.; Gu, Z.-Y.; Chen, Y.-P.; Park, J.; Wei, Z.; Sun, Y.; Bosch, M.; Yuan, S.; Zhou, H.-C. *J. Am. Chem. Soc.* **2014**, *136*, 17714.
- (13) Jiang, H.-L.; Tatsu, Y.; Lu, Z.-H.; Xu, Q. *J. Am. Chem. Soc.* **2010**, *132*, 5586.