Hierarchically Porous MOFs

International Edition: DOI: 10.1002/anie.201610914
German Edition: DOI: 10.1002/ange.201610914

A Modulator-Induced Defect-Formation Strategy to Hierarchically Porous Metal–Organic Frameworks with High Stability

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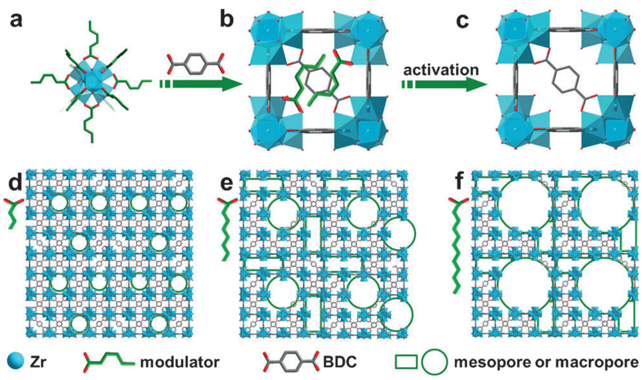
Abstract: *The pore size enlargement and structural stability have been recognized as two crucial targets, which are rarely achieved together, in the development of metal–organic frameworks (MOFs). Herein, we have developed a versatile modulator-induced defect-formation strategy, in the presence of monocarboxylic acid as a modulator and an insufficient amount of organic ligand, successfully realizing the controllable synthesis of hierarchically porous MOFs (HP-MOFs) with high stability and tailorable pore characters. Remarkably, the integration of high stability and large mesoporous property enables these HP-MOFs to be important porous platforms for applications involving large molecules, especially in catalysis.*

Metal–organic frameworks (MOFs) as a relatively new class of porous crystalline materials have attracted intense research interest in recent two decades.[1] The diversity, tailorability, and highly porous character of their structures gives MOFs great potential in multifunctional applications.[1–4] The porosity plays a key role in the structures and functions of MOFs. Although a few mesoporous MOFs have been reported,[5] the pore sizes of MOFs are mainly tunable in a microporous regime, which is actually unfavorable as the small micropore slows down diffusion and restricts the accessibility of large molecules. Hierarchically porous MOFs (HP-MOFs), in which micropores contribute to the high surface area while mesopores/macropores across the micro-porous matrix provide the required accessibility to large molecules for quick diffusion, are highly desired to achieve diverse ends. In addition to the classical methods of extending the length of ligands and/or appropriate assembly between metal clusters and ligands,[5a,c–f] recently HP-MOFs have been developed via different approaches, such as soft-/hard-template or template-free method, stepwise ligand exchange, metal–ligand-fragment co-assembly, imperfect crystallization.[6–8] Unfortunately, most of these approaches are limited to respective synthetic systems that are adaptable to several particular MOFs only and/or they focus on some unstable MOFs.

In fact, most MOFs suffer from framework collapse toward even water/moisture.[2d] Although both large pore sizes and high stability are of great importance toward practical applications of MOFs, unfortunately, the two features are usually contradictory and hardly achieved together in a single MOF. A very limited number of MOFs, such as, MIL-100, MIL-101, PCN-22X series, enlarged UiO structures,[9] which meet both requirements, have received exceptional attention and been intensively studied. However, the tailoring of their pore sizes and porosity is difficult. In this context, the development of reliable methods to obtain stable HP-MOFs with tailored pore structures and tunable properties is imperative but remains a grand challenge.

Herein, we have developed a simple and versatile modulator-induced defect-formation strategy for the rational design and controllable synthesis of various HP-MOFs with exceptional stability, in which pore sizes and pore volumes can be facilely tuned. Different from the traditional synthetic methods, the current HP-MOFs are prepared via reactions between metal precursors and insufficient amounts of ligand, in the presence of monocarboxylic acid as a modulator. The modulator plays a dual role: the carboxylic acid coordinates to the metal ion for the formation of metal–oxo clusters, while the alkyl chain creates structural defects and additional pore space (Scheme 1 a–c), as previously reported for example, for creating spng- and pmg-MOF-5.[8f,h] The pore diameter can be systematically tuned via altering the length and concentration of the modulator (Scheme 1 d–f). To demonstrate the generality of this approach, in addition to the detailed investigations on UiO-66 and its derivatives, different types of HP-MOFs based on stable MIL-53, DUT-5, MOF-808,[10] have also been prepared. It is worth stressing that the stability of these MOFs well remains upon being converted into their hierarchically porous forms. Compared to the pristine MOFs, the resultant



Scheme 1. Schematic illustration of the synthesis of HP-MOFs with adjustable porosity using UiO-66 as an example, see text for details.

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stable HP-MOFs manifest much improved catalytic performance in large-molecule reactions.

The well-established MOF, microporous UiO-66 ($Zr_6O_4(OH)_4(BDC)_6$, BDC = 1,4-benzenedicarboxylate), with high chemical/thermal stability, was firstly investigated, which can be obtained by solvothermal reaction of $ZrCl_4$ and H_2BDC in DMF.[10a] If monocarboxylic acid has been introduced into the reaction system to pre-coordinate to Zr-oxo clusters, a carboxylate ligand (such as H_2BDC) with lower pKa than the monocarboyxlic acid modulator readily replaces the monocarboyxlic acid, and an incomplete exchange would cause structural defects.[11] Inspired by this, we envision that it might be possible to create more and larger structural defects by introducing excess modulator to pre-occupy the coordination sites but an insufficient amount of H_2BDC to only partially replace the modulator. Then the modulator can be removed to release the large pore space to afford hierarchically porous UiO-66 (HP-UiO-66) (Scheme 1 a–c).

The influence of the amount of BDC ligand was examined by using an excess of modulator with Zr/dodecanoic acid of 1:35 and the varying ratios of Zr/BDC from 1:1, 1:0.8, 1:0.5 to 1:0.3 (Figure 1 a,b). When Zr/BDC was 1:1, a ratio for perfect UiO-66, the introduced modulator did not disturb the formation of intact UiO-66, inferring that BDC was able to replace all pre-coordinated modulators. When the ratio was increased to 1:0.8, N_2 sorption isotherm gave a small hysteresis with pore size range extending to 6.8 nm, compared to dominant micropores in the original structure. Further increasing of the ratio to 1:0.5, a pronounced hysteresis loop revealed the typical mesoporous character, in agreement with the pore size distribution of 1–8.6 nm with the peak at 5.5 nm. However, the very high ratio of 1:0.3 led to the small hysteresis and the pore size range was reduced to 5.9 nm with the peak at 3.4 nm. The results clearly show that, the formation of structural defects and mesopores as well as lower surface area is caused by the reduced amount of BDC ligand (optimal Zr/BDC = 1:0.5), a crucial factor to guarantee the generation of the hierarchical pores.

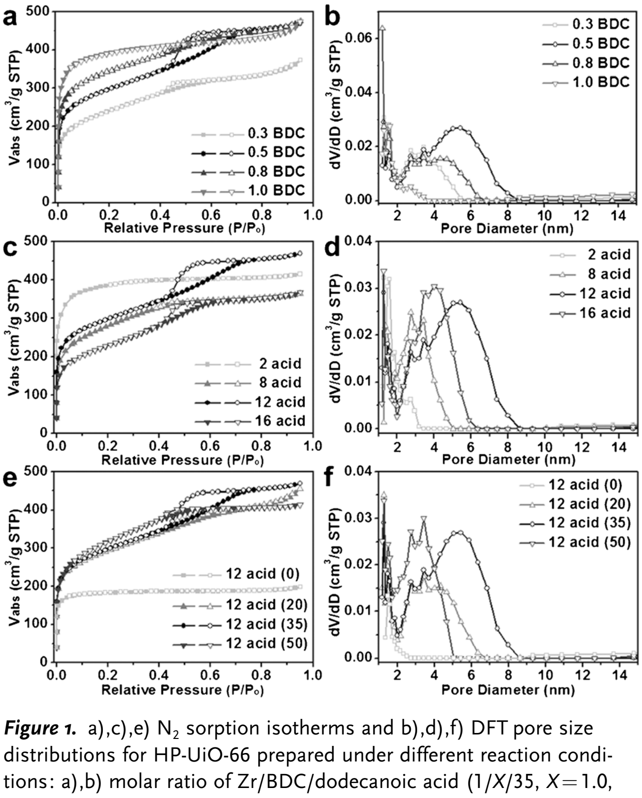

Figure 1. a),c),e) N_2 sorption isotherms and b),d),f) DFT pore size distributions for HP-UiO-66 prepared under different reaction conditions: a),b) molar ratio of Zr/BDC/dodecanoic acid (1/X/35, X = 1.0, 0.8, 0.5, 0.3); c),d) in the presence of various modulators (x acid: x = 2: acetic acid, x = 8: octanoic acid, x = 12: dodecanoic acid, and x = 16: palmitic acid) with a fixed Zr/BDC/modulator ratio of 1/0.5/35; e),f) molar ratio of Zr/BDC/dodecanoic acid (1/0.5/X, X = 0, 20, 35, 50).

To clarify the length influence of the alkyl chain in the modulator, different monocarboxylic acids with varying lengths were introduced, while Zr/BDC ratio was kept to the optimized 1:0.5. Figure 1 c,d show the representative N_2 sorption isotherms and pore size distributions of the resultant UiO-66 and HP-UiO-66 in the presence of acetic acid, octanoic acid, dodecanoic acid and palmitic acid, respectively. When the alkyl chain length is very short, such as acetic acid, the mesopore is hardly generated and thus no obvious mesoporous character can be found in N_2 sorption curves. When the alkyl chain length gradually increases from 8 to 12 carbon atoms, N_2 sorption isotherms of the obtained HP-UiO-66 exhibit accordingly enlarged hysteresis loops. Amongst them, the largest hysteresis loop and pore size up to 8.6 nm (peak at 5.5 nm) can be obtained with dodecanoic acid. The results indicate that the elongated alkyl chain of the modulator could occupy a large space and cause steric hindrance that hampers the coordination between Zr^{IV} and BDC around the long modulator, thus leading to large pores upon the removal of the modulator. However, upon adding the very long palmitic acid with too high pK_a, the pore diameter shrinks instead, possibly owing to the acid's low solubility and weaker coordination with Zr^{IV}.

Knowing that dodecanoic acid is the most suitable modulator, its optimized amount was further examined by altering the feed ratio of Zr/dodecanoic acid. With gradually increased X value in the molar ratio of Zr/BDC/dodecanoic acid = 1/0.5/X, the generated mesopores reached a maximum value at X = 35, followed by a slight decrease (Figure 1 e,f). Note, UiO-66 features micropores only and a low surface area was obtained without modulator, suggesting that the modulator is necessary not only for creating structural defects and additional pore space but also for improving MOF crystallinity and surface area. In other words, the insufficient ligand amount and the presence of suitable modulator are the two pre-requisites for the formation of HP-MOFs. It is proposed that the reaction begins with a rapid formation of the discrete modulator-capped Zr-oxo clusters, which then assembles into the final 3D structure via reversible ligand exchange with the ditopic BDC linker. Owing to the insufficient amount of BDC, the presence of residual modulators makes the structure contain the defects of missing linkers. The defect concentration of the missing linkers is controlled by the amount of BDC and modulator, as well as the alkyl chain length in the modulator. Upon the final removal the modulator by activation, large pores can be generated in the HP-UiO-66.

Based on the above parameters, ideal HP-UiO-66 can be obtained with the optimal recipe of Zr/BDC/dodecanoic acid = 1/0.5/35, the default parameter for HP-UiO-66 hereafter unless otherwise mentioned. Transmission electron microscopy (TEM) observation for HP-UiO-66 clearly shows the worm-like mesopores (Figure S1 in the Supporting Information). The observed smaller pore sizes than those from pore size distribution analysis could be due to the shading/overlay of pore walls in the images[6b] and/or common instability of MOFs exposure to electron beam.[12] It is worth noting that, the emergence of new mesopores in HP-UiO-66 does not significantly affect its intrinsic micropores, as confirmed by the similar surface areas (980 vs. 1204 $m^2 g^{-1}$, respectively for HP-UiO-66 and UiO-66). Intuitively, the abundant defects in the structure would be expected to lead to a weak MOF structure as a result of a lack of ligand support for Zr–oxo clusters making the structure fragile. Unexpectedly, HP-UiO-66 is chemically viable in solutions from concentrated HCl to alkaline solution (pH 12), similar to the pristine UiO-66, as evidenced by powder X-ray diffraction (PXRD) data (Figure 2). The results are encouraging as the MOFs featuring hierarchical pores and high stability are highly sought-after for practical applications in diverse domains.

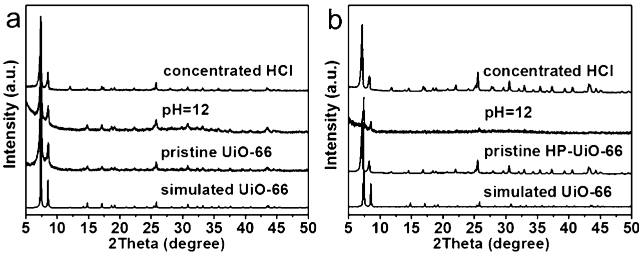

Figure 2. PXRD patterns showing chemical stability of a) UiO-66 and b) HP-UiO-66.

The presence of functional groups on UiO-66 has been demonstrated to be well tolerated in the formation of HP-MOFs. As representatives, H_2BDC-NH_2 and H_2BDC-NO_2 employed in the synthesis have successfully produced HP-UiO-66-NH_2 and HP-UiO-66-NO_2, respectively, evidenced by the hysteresis loops in the N_2 sorption curves and corresponding pore size distributions up to 6 nm (Figures S2 and S3). It is well established that the swapping the BDC ligand in UiO-66 for the longer 4,4′-biphenyldicarboxylic acid (BPDC) gives UiO-67. Likewise, HP-UiO-67 can be obtained by such a modulator-induced approach, featuring large hysteresis loop in its N_2 sorption curves and wide pore size range of 1–12 nm (Figure S4). To our delight, all the functionalized HP-UiO-66 and HP-UiO-67 exhibit high chemical stabilities that are almost identical to their corresponding pristine structures, making them applicable to real-life conditions (Figures S5–S10).

To further illustrate the universality of this synthetic strategy, different types of stable MOFs, including MIL-53, DUT-5, MOF-808, and their functionalized derivatives, have been investigated. Fortunately, following this modulator-induced approach, all their corresponding hierarchically porous structures can be prepared (Figures S11–S25). Similar to the UiO series of MOFs, all these HP-MOFs inherit the very high chemical stability of their parent MOFs (Figures S19–S26). For comparison the porous structural features and stability of the HP-MOFs obtained and their corresponding parent MOFs have been summarized in Table 1 and Table S1.

Table 1: Surface area, pore features, and stability for HP-MOFs.

MOF	S_{BET} [$m^2 g^{-1}$][a]	D_{Meso} [nm][b]	Stability range acid/base
HP-UiO-66	980	5.5	conc.HCl/pH 12
HP-UiO-66-NH_2	789	4.5	conc.HCl/pH 12
HP-UiO-66-NO_2	755	4.3	conc.HCl/pH 12
HP-UiO-67	1948	2-12	pH 1/pH 12
HP-MIL-53	889	5-50	pH 2/pH 10
HP-MIL-53-NH_2	605	2.5-50	pH 2/pH 10
HP-DUT-5	1337	4-50	pH 2/pH 11
HP-MOF-808	453	5-50	conc.HCl/pH 11

[a] BET surface area. [b] Mesopore diameter determined by the density functional theory (DFT) method by N_2 adsorption branch at 77 K.

With highly stable HP-MOFs in our hands, as a proof-of-concept study, we compared the ability of HP-UiO-66 and its parent microporous UiO-66, toward applications involving large molecules. For the encapsulation of functional guest molecules, such as dyes, polyoxometalates, and metalloporphyrins, which are usually larger in sizes than the micropores of MOFs such as UiO-66, HP-UiO-66 unambiguously displays its advantages. As visual evidence, the dye uptake experiments were conducted to confirm that the large pores are involved in uptake by HP-UiO-66. Upon soaking HP-UiO-66 in a DMF solution of coomassie brilliant blue R250 (R250, ca. 2.7 × 1.7 × 0.9 nm in size), the solution gradually faded and the white HP-UiO-66 accordingly turned to brilliant blue. In addition to the large pores (ca. 5.5 nm) in HP-UiO-66, the defect generation might cause the framework to be positively charged, facilitating the trapping of anionic dyes such as R250.[13] In stark contrast, the pristine UiO-66 (window size: ca. 0.6 nm) cannot uptake such a large molecule and its color remains unchanged after even longer soaking time (Figure 3 a).

The incorporation of catalytically active moieties into MOFs is an effective solution to protect them from aggregation and facilitates their dispersion. The in situ incorporation of foreign molecules usually impedes the MOF formation and the post-incorporation after MOF formation poses a prerequisite of large pore sizes. In this case, HP-MOFs create a straightforward approach for the impregnation of large active species into its mesopores while its micropores would merit capillary force. Taking metalloporphyrin, such as Fe-TCPP, as an example of biomimetic catalytic probe, although it almost cannot be adsorbed by the pristine UiO-66 from DMF solution, the HP-UiO-66 with approximately 5.5 nm mesopores was able to efficiently capture the molecule and exhibited fairly good catalytic activity and recyclability (Figure 3 b, and Figures S27, S28).

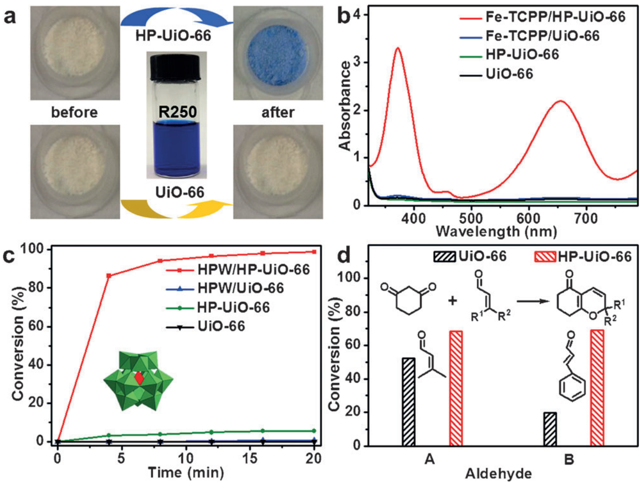

Figure 3. a) Color of the powder samples of UiO-66 and HP-UiO-66 before and after dye adsorption; b) UV/Vis absorption spectra recording the TMB oxidation over different catalysts; c) Time conversion of the ring opening of styrene oxide with methanol over HPW/HP-UiO-66, HPW/UiO-66, HP-UiO-66, and UiO-66; d) Conversion of [3+3] cycloaddition reactions between 1,3-cyclohexanedione and α,β-unsaturated aldehydes over UiO-66 or HP-UiO-66.

As another alternative, the heterogenization of polyoxometalates, a class of excellent acid catalysts, into HP-MOFs was attempted. After soaking UiO-66 and HP-UiO-66 in a methanol solution of phosphotungstic acid (HPW, $H_3PW_{12}O_{40}{\cdot}n\,H_2O$), the catalytic methanolysis of styrene oxide was examined. The resultant HPW-impregnated HP-UiO-66 (HPW/HP-UiO-66) gave significantly higher activity than HP-UiO-66, UiO-66, and HPW-impregnated UiO-66 (HPW/UiO-66) because a higher content of active HPW can be loaded into the HP-UiO-66 (Figure 3c). Moreover, HPW/HP-UiO-66 not only exhibited superior catalytic performance to HPW-loaded UiO-66, even based on a similar HPW loading amount, but also was recyclable without remarkable activity drop, indicative of good stability (Figure S29–S31). In addition to the advantage in the incorporation of large active components, the hierarchical pores facilitate the transport of large substrates/products. The [3+3] cycloaddition reactions between 1,3-cyclohexanedione and various α,β-unsaturated aldehydes of different sizes were investigated (Figure 3d). UiO-66 and HP-UiO-66 gave similar results for small substrates, although UiO-66 showed a slightly lower activity owing to the limited pore size, slow mass diffusion, and even inaccessible active sites, which became much more pronounced when a larger substrate was involved, again demonstrating the superiority of HP-MOFs.

In summary, we have developed a modulator-induced defect-formation strategy to the controllable synthesis of HP-UiO-66 with tailored pore features. The synthetic approach can be adapted to not only functionalized and elongated UiO structures but also a variety of MOFs, suggesting the potential universality for the preparation of HP-MOFs. Particularly, these HP-MOFs effectively integrate the sought-after advantages of high stability and hierarchical pore sizes, after the removal of the modulator (Figure S32–S39). As a result, the HP-MOFs obtained not only are promising as porous platforms for encapsulating large active molecules (such as dyes, polyoxometalates, metalloporphyrins) to give porous functional composites, which primarily manifest their superiority in catalysis, but also exhibit significantly enhanced activity in large-molecule-based reactions compared to the parent microporous MOFs. This versatile synthetic strategy offers an exciting opportunity and paves the way to the preparation of diverse stable MOFs with the combination of intrinsic micropores and additional mesopores or even macropores, which are highly desirable for various real-life applications.

Acknowledgements

We gratefully thank the anonymous reviewers for their valuable suggestions. This work is supported by the NSFC (21371162, 21673213, 21521001, 51301159), the 973 program (2014CB931803), NSF of Anhui Province (1408085MB23), the Recruitment Program of Global Youth Experts, and the Fundamental Research Funds for the Central Universities (WK2060190026, WK2060190065).

Conflict of interest

The authors declare no conflict of interest.

Keywords: heterogeneous catalysis · hierarchically porous materials · large molecules · metal–organic frameworks · stability

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[1] a) J. R. Long, O. M. Yaghi, *Chem. Soc. Rev.* **2009**, *38*, 1213; b) H.-C. Zhou, J. R. Long, O. M. Yaghi, *Chem. Rev.* **2012**, *112*, 673; c) H.-C. Zhou, S. Kitagawa, *Chem. Soc. Rev.* **2014**, *43*, 5415.

[2] a) J. Liu, P. K. Thallapally, B. P. McGrail, D. R. Brown, J. Liu, *Chem. Soc. Rev.* **2012**, *41*, 2308; b) J.-R. Li, J. Sculley, H.-C. Zhou, *Chem. Rev.* **2012**, *112*, 869; c) P.-Q. Liao, W.-X. Zhang, J.-P. Zhang, X.-M. Chen, *Nat. Commun.* **2015**, *6*, 8697; d) W. Zhang, Y. Hu, J. Ge, H.-L. Jiang, S.-H. Yu, *J. Am. Chem. Soc.* **2014**, *136*, 16978.

[3] a) D. Farrusseng, S. Aguado, C. Pinel, *Angew. Chem. Int. Ed.* **2009**, *48*, 7502; *Angew. Chem.* **2009**, *121*, 7638; b) H.-L. Jiang, Q. Xu, *Chem. Commun.* **2011**, *47*, 3351; c) L. E. Kreno, K. Leong, O. K. Farha, M. Allendorf, R. P. Van Duyne, J. T. Hupp, *Chem. Rev.* **2012**, *112*, 1105; d) H. Kitagawa, *Nat. Chem.* **2009**, *1*, 689; e) J. Liu, L. Chen, H. Cui, J. Zhang, L. Zhang, C.-Y. Su, *Chem. Soc. Rev.* **2014**, *43*, 6011.

[4] a) B. Chen, S. Xiang, G. Qian, *Acc. Chem. Res.* **2010**, *43*, 1115; b) Y. Yan, M. Suyetin, E. Bichoutskaia, A. J. Blake, D. R. Allan, S. A. Barnett, M. Schröder, *Chem. Sci.* **2013**, *4*, 1731; c) Z. Hu, B. J. Deibert, J. Li, *Chem. Soc. Rev.* **2014**, *43*, 5815; d) Y. Liu, Z. Tang, *Adv. Mater.* **2013**, *25*, 5819; e) C. K. Brozek, M. Dincă, *Chem. Sci.* **2012**, *3*, 2110; f) A. Mallick, B. Garai, D. D. Díaz, R. Banerjee, *Angew. Chem. Int. Ed.* **2013**, *52*, 13755; *Angew. Chem.* **2013**, *125*, 14000; g) Z. Hu, D. Zhao, *Dalton Trans.* **2015**, *44*, 19018; h) M. S. Denny, S. M. Cohen, *Angew. Chem. Int. Ed.* **2015**, *54*, 9029; *Angew. Chem.* **2015**, *127*, 9157; i) W.-Y. Gao, M. Chrzanowski, S. Ma, *Chem. Soc. Rev.* **2014**, *43*, 5841; j) T. K. Kim, K. J. Lee, J. Y. Cheon, J. H. Lee, S. H. Joo, H. R. Moon, *J. Am. Chem. Soc.* **2013**, *135*, 8940.

[5] a) K. Koh, A. G. Wong-Foy, A. J. Matzger, *Angew. Chem. Int. Ed.* **2008**, *47*, 677; *Angew. Chem.* **2008**, *120*, 689; b) A. Sonnauer, F. Hoffmann, M. Fröba, L. Kienle, V. Duppel, M. Thommes, C. Serre, G. Férey, N. Stock, *Angew. Chem. Int. Ed.* **2009**, *48*, 3791; *Angew. Chem.* **2009**, *121*, 3849; c) N. Klein, I. Senkovska, K. Gedrich, U. Stoeck, A. Henschel, U. Mueller, S. Kaskel, *Angew. Chem. Int. Ed.* **2009**, *48*, 9954; *Angew. Chem.* **2009**, *121*, 10139; d) H. Deng, S. Grunder, K. E. Cordova, C. Valente, H. Furukawa, M. Hmadeh, F. Gándara, A. C. Whalley, Z. Liu, S. Asahina, H. Kazumori, M. O'Keeffe, O. Terasaki, J. F. Stoddart, O. M. Yaghi, *Science* **2012**, *336*, 1018; e) W. Xuan, C. Zhu, Y. Liu, Y. Cui, *Chem. Soc. Rev.* **2012**, *41*, 1677; f) P.-Z. Li, X.-J. Wang, S. Y. Tan, C. Y. Ang, H. Chen, J. Liu, R. Zou, Y. Zhao, *Angew. Chem. Int. Ed.* **2015**, *54*, 12748; *Angew. Chem.* **2015**, *127*, 12939.

[6] a) L. Qiu, T. Xu, Z. Li, W. Wang, Y. Wu, X. Jiang, X. Tian, L. Zhang, *Angew. Chem. Int. Ed.* **2008**, *47*, 9487; *Angew. Chem.* **2008**, *120*, 9629; b) L.-B. Sun, J.-R. Li, J. Park, H.-C. Zhou, *J. Am. Chem. Soc.* **2012**, *134*, 126; c) S. Cao, G. Gody, W. Zhao, S. Perrier, X. Peng, C. Ducati, D. Zhao, A. K. Cheetham, *Chem. Sci.* **2013**, *4*, 3573.

[7] a) Y. Wu, F. Li, W. Zhu, J. Cui, C. Tao, C. Lin, P. M. Hannam, G. Li, *Angew. Chem. Int. Ed.* **2011**, *50*, 12518; *Angew. Chem.* **2011**, *123*, 12726; b) J. Reboul, S. Furukawa, N. Horike, M. Tsotsalas, K. Hirai, H. Uehara, M. Kondo, N. Louvain, O. Sakata, S. Kitagawa, *Nat. Mater.* **2012**, *11*, 717; c) W. Zhang, Y. Liu, G. Lu, Y. Wang, S. Li, C. Cui, J. Wu, Z. Xu, D. Tian, W. Huang, J. S. DuCheneu, W. D. Wei, H. Chen, Y. Yang, F. Huo, *Adv. Mater.* **2015**, *27*, 2923; d) H. Huang, J.-R. Li, K. Wang, T. Han, M. Tong, L. Li, Y. Xie, Q. Yang, D. Liu, C. Zhong, *Nat. Commun.* **2015**, *6*, 8847.

[8] a) Y. Yue, Z. Qiao, P. F. Fulvio, A. J. Binder, C. Tian, J. Chen, K. M. Nelson, X. Zhu, S. Dai, *J. Am. Chem. Soc.* **2013**, *135*, 9572; b) Y. Zhao, J. Zhang, B. Han, J. Song, J. Li, Q. Wang, *Angew. Chem. Int. Ed.* **2011**, *50*, 636; *Angew. Chem.* **2011**, *123*, 662; c) L. Peng, J. Zhang, Z. Xue, B. Han, X. Sang, C. Liu, G. Yang, *Nat. Commun.* **2014**, *5*, 5465; d) T. Li, M. T. Kozlowski, E. A. Doud, M. N. Blakely, N. L. Rosi, *J. Am. Chem. Soc.* **2013**, *135*, 11688; e) J. Park, L. Sun, Y. Chen, H.-C. Zhou, *J. Am. Chem. Soc.* **2012**, *134*, 20110; f) K. M. Choi, H. J. Jeon, J. K. Kang, O. M. Yaghi, *J. Am. Chem. Soc.* **2011**, *133*, 11920; g) Y. Kim, T. Yang, G. Yun, M. B. Ghasemian, J. Koo, E. Lee, S. Cho, K. Kim, *Angew. Chem. Int. Ed.* **2015**, *54*, 13273; *Angew. Chem.* **2015**, *127*, 13471; h) S. He, Y. Chen, Z. Zhang, B. Ni, W. He, X. Wang, *Chem. Sci.* **2016**, *7*, 7101.

[9] a) G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surblé, I. Margiolaki, *Science* **2005**, *309*, 2040; b) P. Horcajada, S. Surblé, C. Serre, D.-Y. Hong, Y.-K. Seo, J.-S. Chang, J.-M. Grenèche, I. Margiolaki, G. Férey, *Chem. Commun.* **2007**, 2820; c) A. Schaate, P. Roy, A. Godt, J. Lippke, F. Waltz, M. Wiebcke, P. Behrens, *Chem. Eur. J.* **2011**, *17*, 6643; d) D. Feng, Z.-Y. Gu, J.-R. Li, H.-L. Jiang, Z. Wei, H.-C. Zhou, *Angew. Chem. Int. Ed.* **2012**, *51*, 10307; *Angew. Chem.* **2012**, *124*, 10453.

[10] a) J. H. Cavka, S. Jakobsen, U. Olsbye, N. Guillou, C. Lamberti, S. Bordiga, K. P. Lillerud, *J. Am. Chem. Soc.* **2008**, *130*, 13850; b) M. Kandiah, M. H. Nilsen, S. Usseglio, S. Jakobsen, U. Olsbye, M. Tilset, C. Larabi, E. A. Quadrelli, F. Bonino, K. P. Lillerud, *Chem. Mater.* **2010**, *22*, 6632; c) T. Loiseau, C. Serre, C. Huguenard, G. Fink, F. Taulelle, M. Henry, T. Bataille, G. Férey, *Chem. Eur. J.* **2004**, *10*, 1373; d) T. Ahnfeldt, D. Gunzelmann, T. Loiseau, D. Hirsemann, J. Senker, G. Férey, N. Stock, *Inorg. Chem.* **2009**, *48*, 3057; e) I. Senkovska, F. Hoffmann, M. Fröba, J. Getzschmann, W. Böhlmann, S. Kaskel, *Microporous Mesoporous Mater.* **2009**, *122*, 93; f) H. Furukawa, F. Gándara, Y.-B. Zhang, J. Jiang, W. L. Queen, M. R. Hudson, O. M. Yaghi, *J. Am. Chem. Soc.* **2014**, *136*, 4369.

[11] a) H. Wu, Y. S. Chua, V. Krungleviciute, M. Tyagi, P. Chen, T. Yildirim, W. Zhou, *J. Am. Chem. Soc.* **2013**, *135*, 10525; b) F. Vermoortele, B. Bueken, G. Le Bars, B. Van de Voorde, M. Vandichel, K. Houthoofd, A. Vimont, M. Daturi, M. Waroquier, V. Van Speybroeck, C. Kirschhock, D. E. De Vos, *J. Am. Chem. Soc.* **2013**, *135*, 11465; c) Z. Fang, B. Bueken, D. E. De Vos, R. A. Fischer, *Angew. Chem. Int. Ed.* **2015**, *54*, 7234; *Angew. Chem.* **2015**, *127*, 7340; d) C. A. Trickett, K. J. Gagnon, S. Lee, F. Gándara, H.-B. Bürgi, O. M. Yaghi, *Angew. Chem. Int. Ed.* **2015**, *54*, 11162; *Angew. Chem.* **2015**, *127*, 11314.

[12] R. J. T. Houk, B. W. Jacobs, F. E. Gabaly, N. N. Chang, A. A. Talin, D. D. Graham, S. D. House, I. M. Robertson, M. D. Allendorf, *Nano Lett.* **2009**, *9*, 3413.

[13] X. Zhao, C. Mao, K. T. Luong, Q. Lin, Q.-G. Zhai, P. Feng, X. Bu, *Angew. Chem. Int. Ed.* **2016**, *55*, 2768; *Angew. Chem.* **2016**, *128*, 2818.

Manuscript received: November 8, 2016
Final Article published: ■■ ■■, ■■■■

Communications

Hierarchically Porous MOFs

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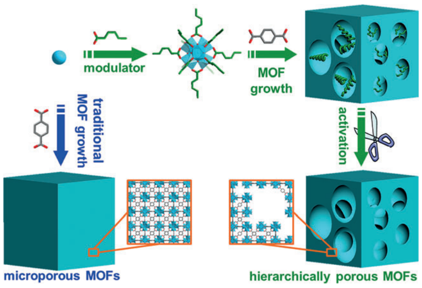
A Modulator-Induced Defect-Formation Strategy to Hierarchically Porous Metal–Organic Frameworks with High Stability



Cause and defect: Pore size enlargement and structural stability are two crucial targets but hardly achieved together in metal–organic frameworks (MOFs). A versatile modulator-induced defect-formation strategy has been developed to provide hierarchically porous MOFs (HP-MOFs) with high stability and tailorable pore characters, which are important porous platforms for large molecule-involved applications, especially in catalysis.