Pore size expansion ...

... and framework stability are two crucial issues, but are rarely addressed simultaneously in a single metal–organic framework (MOFs). H.-L. Jiang and G. Cai show in their Communication on page 567 ff. that a versatile modulator-induced defect-formation strategy allows the preparation of hierarchically porous MOFs (HP-MOFs) with high stability and tailorable pore features, which enable HP-MOFs to be important porous platforms for applications involving large molecules, especially in catalysis.
Hierarchically Porous MOFs

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

Guorui Cai and Hai-Long Jiang*

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–e] 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.[5a–e] 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.[5f] 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 1a–c), as previously reported for example, for creating spg- and pmg-MOF-5.[10a] The pore diameter can be systematically tuned via altering the length and concentration of the modulator (Scheme 1d–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,[10b] 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...
stable HP-MOFs manifest much improved catalytic performance in large-molecule reactions.

The well-established MOF, microporous UiO-66 (Zr(III)O(OH)(BDC)), BDC = 1,4-benzenedicarboxylate), with high chemical/thermal stability, was firstly investigated, which can be obtained by solvothermal reaction of ZrCl₄ and H₂BDC in DMF. If monocarboxylic acid has been introduced into the reaction system to pre-coordinate to Zr-oxo clusters, a carboxylate ligand (such as H₂BDC) with lower pKa than the monocarboxylic acid modulator readily replaces the monocarboxylic acid, and an incomplete exchange would cause structural defects. 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 H₂BDC 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 1a–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 1a,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, N₂ sorption isotherm gave a small hysteresis with pore size range extending to 6.8 nm, compared to the optimized 1:0.5. Figure 1c,d show the representative N₂ 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 N₂ sorption curves. When the alkyl chain length gradually increases from 8 to 12 carbon atoms, N₂ 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 Zr⁴⁺ 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 pKa, the pore diameter shrinks instead, possibly owing to the acid’s low solubility and weaker coordination with Zr⁴⁺.

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 1e,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.

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 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 3a).

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 3b, and Figures S27, S28).

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

<table>
<thead>
<tr>
<th>MOF</th>
<th>$S_{BET}$ [m$^2$ g$^{-1}$]</th>
<th>$D_{Meso}$ [nm]$^4$</th>
<th>Stability range acid/base</th>
</tr>
</thead>
<tbody>
<tr>
<td>HP-Uio-66</td>
<td>980</td>
<td>5.5</td>
<td>conc.HCl/pH 12</td>
</tr>
<tr>
<td>HP-Uio-66-NH$_2$</td>
<td>789</td>
<td>4.5</td>
<td>conc.HCl/pH 12</td>
</tr>
<tr>
<td>HP-Uio-66-NO$_2$</td>
<td>755</td>
<td>4.3</td>
<td>conc.HCl/pH 12</td>
</tr>
<tr>
<td>HP-Uio-67</td>
<td>1948</td>
<td>2.12</td>
<td>pH 1/pH 12</td>
</tr>
<tr>
<td>HP-Mil-53</td>
<td>889</td>
<td>5-50</td>
<td>pH 2/pH 10</td>
</tr>
<tr>
<td>HP-Mil-53-NH$_2$</td>
<td>605</td>
<td>2.5-50</td>
<td>pH 2/pH 10</td>
</tr>
<tr>
<td>HP-DUT-5</td>
<td>1337</td>
<td>4-50</td>
<td>pH 2/pH 11</td>
</tr>
<tr>
<td>HP-MOF-808</td>
<td>453</td>
<td>5-50</td>
<td>conc.HCl/pH 11</td>
</tr>
</tbody>
</table>

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

![Figure 2. PXRD patterns showing chemical stability of a) Uio-66 and b) HP-Uio-66.](image)
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, H₃PW₁₂O₄H₂O), the catalytic methanlysis of styrene oxide was examined. The resultant HPW-impregnated HP-Uio-66 (HPW/HP-Uio-66) give 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 over UiO-66 or HP-Uio-66.

**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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