Supporting Information

Uncovering Two Principles of Multivariate Hierarchical Metal-Organic Framework Synthesis via Retrosynthetic Design

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S1. Materials and Instrumentation

All reagents and solvents were commercially available and used as received.

**N₂ sorption isotherm.** Gas sorption measurements were conducted using a Micromeritics ASAP 2020 system. Prior to gas sorption measurements, about 100 mg MOF materials were washed thoroughly with DMF and exchanged by chloroform for 3 days, during which the solvent was decanted and freshly replenished three times every day. The solvent was then removed under vacuum at 100°C for 12 h, yielding porous material.

**Powder X-ray diffraction (PXRD).** PXRD was carried out with a Bruker D8-Focus Bragg-Brentano X-ray Powder Diffractometer equipped with a Cu sealed tube (λ = 1.54178 Å) at 40 kV and 40 mA.

**¹H NMR spectroscopy.** Nuclear magnetic resonance (NMR) data were collected on an Inova 500 spectrometer. For ¹H NMR spectroscopy, the activated samples (around 10 mg) were dissolved in 600 µL DMSO-d₆ solution containing 20 µL HF.

**Thermogravimetric Analysis (TGA).** About 10 mg of the sample was heated on a TGA Q500 thermogravimetric analyzer from room temperature to 600 °C at a rate of 5°C·min⁻¹ under air flow of 20 mL·min⁻¹.

**Scanning electron microscopy (SEM).** Images and analyses of SEM/EDX were taken by FEI Quanta 600 FE-SEM. The Quanta 600 FEG is a field emission scanning electron microscope capable of generating and collecting high-resolution and low-vacuum images. It is equipped with a motorized x-y-z-tilt-rotate stage, providing the following movements: x = y = 150 mm (motorized); z = 65 mm (motorized); Tilt +70 degrees to −5 degrees (motorized); Source: Field emission gun assembly with Schottky emitter source. Voltage: 200 V to 30 kV. Beam Current: >100 nA.

**ICP-MS Analysis.** Calibration standards were prepared from certified reference standards from RICCA Chemical Company. Samples were further analyzed with a Perkin Elmer NexION® 300D ICP-MS. Resulting calibration curves have minimum \( R^2 = 0.9999 \). Additionally, in order to maintain accuracy, quality control samples from certified reference standards and internal standards were utilized. The individual results of the triplicate samples were averaged to determine the metal concentration.

**Confocal laser scanning microscopy (CLSM).** CLSM images were performed on an Olympus FV1000-IX81 CLSM and a Leica TCS SP confocal system (Leica, Germany).

S2. Preparation and Characterization of PCN-222@MOF-5

S2.1 General synthetic condition for hierarchical MOFs. Relative stable core MOFs were placed in the precursor solution containing linkers of shell MOFs. After the linker
preloading and surface functionalization, solution containing metals of shell MOFs was added into the mixtures, allowing the formation of shell MOFs outside core MOFs.

Figure S1. Structural illustration of various metal-organic frameworks (MOFs) including MOF-5 (a,b), MOF-5-NH$_2$ (c), MOF-5-BPDC (d, interpenetrated framework), HKUST-1 (e), MIL-125 (f), UiO-66 (g), and PCN-222 (h). Note that MOF-5, MOF-5-NH$_2$ and MOF-5-BPDC are isoreticular (IR) MOFs, while only MOF-5-BPDC has an interpenetrated framework (shown as the orange lattice in d).

S2.2 Synthesis of MOF-5. MOF-5 was synthesized on the basis of previous reports with slight modifications.$^{1}$ Zn(NO$_3$)$_2$·6H$_2$O (41.6 mg), BDC (8.8 mg) and DEF (2 mL) were charged in a Pyrex vial. The mixture was heated in an 85 °C oven for 24 h to generate the cubic crystals of MOF-5. The crystals of MOF-5 were collected by centrifugation and washed with fresh DMF for 3 times. Synthesis of MOF-5 under 100 °C also generates similar cubic crystals.

Figure S2. Microscopic images of MOF-5 crystals.
Figure S3. SEM images of MOF-5.

**S2.3 Synthesis of PCN-222.** PCN-222(No Metal) was synthesized on the basis of previous reports with slight modifications. ZrCl$_4$ (70 mg), TCPP (50 mg) and benzoic acid (2700 mg) in N,N-diethylformamide (8 mL) were ultrasonically dissolved in a 20 mL Pyrex vial. The mixture was heated at 120 °C in an oven for 48 h. After cooling down to room temperature, needle-shaped crystals were harvested by filtration.

Figure S4. SEM images and PXRD patterns of PCN-222.

**S2.4 Synthesis of PCN-222(Zn)/MOF-5.** Activated PCN-222 (10 mg), Zn(NO$_3$)$_2$·6H$_2$O (41.6 mg), BDC (8.8 mg) and DEF (2 mL) were charged in a Pyrex vial. The mixture was heated in an 85 °C oven for 24 h. The formation of MOF-5 cubic crystals was observed as a separated phase.
Figure S5. Microscopic images of PCN-222/MOF-5 crystals synthesized without surface functionalization. Both (a) region 1 and (b) region 2 of PCN-222/MOF-5 indicate the separated growth of MOF-5 in the presence of PCN-222.

**S2.5 Synthesis of PCN-222(Zn)@MOF-5-(1%).** Activated PCN-222 (3 mg), BDC (8.8 mg) and DEF (1 mL) were charged in a Pyrex vial. The mixture was heated in an 85 °C oven for 24 h. Zn(NO$_3$)$_2$·6H$_2$O (41.6 mg) and DEF (1 mL) were further added into the vial. The mixture was heated in an 85 °C oven for 24 h to generate the crystals of PCN-222(Zn)@MOF-5-(1%). The crystals were collected by centrifugation and washed with fresh DMF for 3 times. The ratio of ZnTCPP and BDC in MOFs was calculated by $^1$H-NMR spectra. Molar ratio based on integration of the peaks: ZnTCPP: BDC = 1: 129.77.

**S2.6 Synthesis of PCN-222(Zn)@MOF-5-(8%).** Activated PCN-222 (12 mg), BDC (8.8 mg) and DEF (1 mL) were charged in a Pyrex vial. The mixture was heated in an 85 °C oven for 24 h. Zn(NO$_3$)$_2$·6H$_2$O (41.6 mg) and DEF (1 mL) were further added into the vial. The mixture was heated in an 85 °C oven for 24 h to generate the crystals of PCN-222(Zn)@MOF-5-(8%). The crystals were collected by centrifugation and washed with fresh DMF for 3 times. The ratio of ZnTCPP and BDC in MOFs was calculated by $^1$H-NMR spectra. Molar ratio based on integration of the peaks: ZnTCPP: BDC = 1: 17.18.
Figure S6. SEM images and corresponding SEM-EDS mapping of the surface (a) and interior (b) of PCN-222@MOF-5-(8%); (c) Corresponding metal ratio (mol%) calculated from SEM-EDS mapping and ICP-MS. The internal areas of PCN-222@MOF-5-(8%) was accessed by simply crushing. Note that the uneven O distribution on SEM-EDS (b) is caused by the shadowing effects related to the rough internal surface of the crushed sample. When scattered by X-rays at a single point, the nearby hill obstructs the X-rays from being detected by the EDS detector. Further complexities occur when surfaces are inclined towards the detector in a considerable degree while other surfaces are sloping away, especially for elements including C and O. For comparison, other EDS figures (i.e. Figure S6a) with relative flat surface will show better dispersion of O on the surface, with only negligible shadowing effects observed. Although EDS might not be able to provide a highly accurate distribution analysis on the atomic apportionment in hierarchical MOFs, it provides a reference to visualize the approximate distribution. More importantly, morphology analysis can be utilized to understand the distribution, because the needle-like PCN-222 and large cubic-like MOF-5 can be easily distinguished from SEM images.
Figure S7. SEM images and corresponding SEM-EDS mapping of hierarchical PCN-222@MOF-5-(8%). (a-b) SEM images of the surface of MOF-5 crystals, clearly showing the presence of needle-like PCN-222 on the surface; (c-d) SEM images of hierarchical PCN-222@MOF-5-(8%) that was cut off to exhibit the internal arrangement of PCN-222 needle crystals; (e-g) SEM images and corresponding SEM-EDS mapping of hierarchical PCN-222@MOF-5-(8%) that was pressed and destroyed by a silicon plate to show the presence of PCN-222 within MOF-5 crystals. After the hierarchical MOFs were pressed, needle-like PCN-222 could be easily distinguished by the morphology (highlighted in yellow rectangles), while the template effects of PCN-222 inside hierarchical PCN-222@MOF-5-(8%) could also be observed by the holes.
after crushing (highlighted in yellow circles).

Figure S8. Confocal laser scanning microscopy (CLSM) images of hierarchical PCN-222(Zn)@MOF-5-8%: (a) fluorescence; (b) bright field. CLSM z-stack 3D-model images of the PCN-222(Zn)@MOF-5-8% crystal with various rotation angles (c) 0°; (d) 45°; (e) 90° and (f) 180°. CLSM images reveal that PCN-222(Zn) nanocrystals are distributed throughout the bulk of MOF-5 macrocrystals (>100 μm size), as indicated by the fluorescence behavior of PCN-222(Zn).

S2.7 Synthesis of PCN-222(Zn)@MOF-5-(14%). Activated PCN-222 (20 mg), BDC (8.8 mg) and DEF (1 mL) were charged in a Pyrex vial. The mixture was heated in an 85 ºC oven for 24 h. Zn(NO$_3$)$_2$·6H$_2$O (41.6 mg) and DEF (1 mL) were further added into the vial. The mixture was heated in an 85 ºC oven for 24 h to generate the crystals of PCN-222(Zn)@MOF-5-(14%). The crystals were collected by centrifugation and washed with fresh DMF for 3 times. The ratio of ZnTCPP and BDC in MOFs was calculated by $^1$H-NMR spectra. Molar ratio based on integration of the peaks: ZnTCPP: BDC = 1: 8.86.

S2.8 Synthesis of center-concentrated PCN-222(Zn)@MOF-5. Higher concentration of MOF-5 precursor was utilized to synthesize core-shell PCN-222(Zn)@MOF-5. Activated PCN-222 (20 mg), BDC (17.6 mg) and DEF (1 mL) were charged in a Pyrex vial. The mixture was heated in an 85 ºC oven for 24 h. Zn(NO$_3$)$_2$·6H$_2$O (83.2 mg) and DEF (1 mL) were further added into the vial. The mixture was heated in an 85 ºC oven for 24 h to generate the crystals of PCN-222(Zn)@MOF-5. The crystals of PCN-222(Zn)@MOF-5 were collected by
centrifugation and washed with fresh DMF for 3 times. The ratio of ZnTCPP and BDC in MOFs was calculated by $^1\text{H}$-NMR spectra.

Figure S9. SEM images of core-shell PCN-222@MOF-5.

**S2.9 Synthesis of PCN-222-CA@MOF-5.** Activated PCN-222 (5 mg), citric acid (CA, 20 mg) and DEF (2 mL) were charged in a Pyrex vial. The mixture was heated in an 85 °C oven for 24 h. After cooling down to room temperature, the crystals of CA functionalized PCN-222 were harvested and washed thoroughly with DMF. PCN-222-CA (5 mg), Zn(NO$_3$)$_2$$\cdot$6H$_2$O (41.6 mg), BDC (8.8 mg) and DEF (2 mL) were charged in a Pyrex vial. The mixture was heated in an 85 °C oven for 24 h. The formation of MOF-5 cubic crystals was observed as a separated phase.

Figure S10. PXRD patterns of PCN-222-CA@MOF-5.
S2.10 Composition investigation of hierarchical MOFs (PCN-222@MOF-5). The composition was analyzed through $^1$H NMR of digested hierarchical MOFs. In general, the activated samples (around 10 mg) were dissolved in 600 µL DMSO-$d_6$ solution containing 20 µL HF. The digestion solution was used directly for $^1$H-NMR on an Inova 500 spectrometer.

Figure S11. SEM images and EDS element mapping of PCN-222-CA@MOF-5.

Figure S12. $^1$H NMR spectroscopy of digested PCN-222@MOF-5-(1%).
Figure S13. $^1$H NMR spectroscopy of digested PCN-222@MOF-5-(8%).

Figure S14. $^1$H NMR spectroscopy of digested PCN-222@MOF-5-(14%).
Table S1. Approximate composition of PCN-222@MOF-5.

| Sample Name       | Average Composition                                                                 |
|-------------------|--------------------------------------------------------------------------------------|
| PCN-222           | Zr₆(µ₃-O)₄(µ₃-OH)₄(OH)₄(H₂O)₄(ZnTCPP)₂                                               |
| MOF-5             | Zn₄O(BDC)₃                                                                            |
| PCN-222@MOF-5(14%)| [Zr₆(µ₃-O)₄(µ₃-OH)₄(OH)₄(H₂O)₄(ZnTCPP)₂]₁ [Zn₄O(BDC)₃]₅.9                          |
| PCN-222@MOF-5(8%) | [Zr₆(µ₃-O)₄(µ₃-OH)₄(OH)₄(H₂O)₄(ZnTCPP)₂]₁ [Zn₄O(BDC)₃]₁₁.5                         |
| PCN-222@MOF-5(1%) | [Zr₆(µ₃-O)₄(µ₃-OH)₄(OH)₄(H₂O)₄(ZnTCPP)₂]₁ [Zn₄O(BDC)₃]₈₆.5                         |

Figure S15. The full DRIFTS spectra of MOF-5, PCN-222@MOF-5-8%, PCN-222@MOF-5-14% and PCN-222. The presence of PCN-222 in the hierarchical PCN-222@MOF-5 can be confirmed by the DRIFTS spectra. From the spectra of hierarchical PCN-222@MOF-5-8% and PCN-222@MOF-5-14%, we are able to observe the peaks corresponding to the porphyrin ring vibrations around 1500-1600 cm⁻¹ and 1200 cm⁻¹. Also, the OH groups on the defective Zr₆ clusters in PCN-222 have IR absorption bands around 3667 cm⁻¹. These peaks can also be observed in the hierarchical PCN-222@MOF-5-8% and PCN-222@MOF-5-14%.
Figure S16. Illustration of the importance of surface functionalization during the preparation of hierarchical MTV-MOFs. (a) Without surface functionalization, the MOF-5 prefers to form as a separate phase during nucleation and growth process, due to the lattice mismatching. (b) With surface functionalization of PCN-224 with citric acid, the coordination compounds prefer to attach on the surface of PCN-224 and grow into hierarchical structures. (c) With preloaded linkers inside PCN-224 pores, the surface functionalization and slow releasing of linkers to the interface would allow the formation of new MOFs outside the core MOFs. All these comparison experiments show that surface functionalization is one of the prerequisites during hierarchical MOF synthesis.
S3. Versality of Hierarchical MOF Synthesis

S3.1 Combination of hierarchical MOFs

Figure S17. Construction of multivariate hierarchical MOFs under the guidance of retrosynthetic design. Combinatorics was utilized to predict the possibility of hierarchical MOF structures, containing multiply metal clusters and linkers with different connectivities. To simplify the question, we assume that each MOF only has one type of linker and cluster, and do not consider mixed-linker or –cluster cases. During the calculation, one prerequisite is that the more stable cluster should always be in the inner layer of hierarchical MOFs while more labile cluster should always be in the outer layer of hierarchical MOFs. There is no limitation on the linker arrangement. If we select k clusters from a library of n types of clusters and linked them to m types of linkers to obtain hierarchical core-shell MOFs, the number of total structures would be:

$$\text{Total structures} = m^k \cdot C(n, k) = m^k \cdot \frac{n!}{k!(n-k)!}$$
Figure S18. Conceptual illustration of stepwise construction of multivariate hierarchical MTV-MOFs under the guidance of retrosynthetic design. (a) To obtain a desired MTV-MOF, the stepwise synthesis, starting from the more stable bonds to more labile bonds, should rationally be carried out. Metal–carboxylate bond strengths with a given ligand are proportional to the charges of the metal cations while they are inversely proportional to the ionic radius. Therefore, by checking the strength of the bonds that form the framework, we can roughly predict the stability of MOFs. It is believed that when it comes to metal–carboxylate frameworks, high-valent metal ions possessing higher charge densities can form stronger coordination bonds, leading to a more stable framework. The ligand exchange constant is an important factor to access hydrothermal stability of MOFs. If the MOF clusters have lower ligand exchange constants, the resulting MOFs are typically more stable (Table S2). (b) To obtain a desired MTV hierarchical MOF, the stepwise synthesis, starting from the center to surface, can also be rationally carried out.
Table S2. Water exchange rate constants (25°C).  

| M(nL)\((\text{OH})_n\) | k (s\(^{-1}\)) |
|------------------------|----------------|
| Cu(\((\text{OH})_2\))\(^{2+}\) | 4.4 x 10\(^9\) |
| Zn(\((\text{OH})_2\))\(^{2+}\) | > 10\(^7\) |
| Yb(\((\text{OH})_2\))\(^{3+}\) | > 10\(^7\) |
| Fe(\((\text{OH})_2\))\(^{2+}\) | 4.4 x 10\(^6\) |
| Co(\((\text{OH})_2\))\(^{2+}\) | 3.2 x 10\(^6\) |
| Ni(\((\text{OH})_2\))\(^{2+}\) | 3.2 x 10\(^4\) |
| Fe(\((\text{OH})_2\))\(^{3+}\) | 1.6 x 10\(^2\) |
| Al(\((\text{OH})_2\))\(^{3+}\) | 1.3 |
| Cr(\((\text{OH})_2\))\(^{3+}\) | 2.4 x 10\(^{-6}\) |

S3.2 Synthesis of shell MOFs
S3.2.1 Synthesis of MOF-5-NH\(_2\). MOF-5-NH\(_2\) was synthesized according to the literature with slight modification.\(^1\) Zn(NO\(_3\))\(_2\)·6H\(_2\)O (41.6 mg), H\(_2\)BDC-NH\(_2\) (10 mg) and DEF (2 mL) were charged in a Pyrex vial. The mixture was heated in a 100 °C oven for 24 h to generate the cubic crystals of MOF-5-NH\(_2\). The crystals of MOF-5-NH\(_2\) were collected by centrifugation and washed with fresh DMF for 3 times.

![Microscopic images of MOF-5-NH\(_2\) crystals.](image)

S3.2.2 Synthesis of MOF-5-Br. MOF-5-Br was synthesized according to the literature with slight modification.\(^5\) Zn(NO\(_3\))\(_2\)·6H\(_2\)O (41.6 mg), H\(_2\)BDC-Br (10 mg) and DEF (2 mL) were charged in a Pyrex vial. The mixture was heated in a 100 °C oven for 24 h to generate the cubic crystals of MOF-5-Br. The crystals of MOF-5-Br were collected by centrifugation and washed with fresh DMF for 3 times.

S3.2.3 Synthesis of MOF-5-1,4-NDC. MOF-5-1,4-NDC was synthesized according to...
the literature with slight modification.\textsuperscript{5} Zn(NO$_3$)$_2$·6H$_2$O (41.6 mg), 1,4- H$_2$NDC (12 mg) and DEF (2 mL) were charged in a Pyrex vial. The mixture was heated in a 100 °C oven for 24 h to generate the cubic crystals of MOF-5-1,4-NDC. The crystals of MOF-5-1,4-NDC were collected by centrifugation and washed with fresh DMF for 3 times.

**S3.2.4 Synthesis of MOF-5-BPDC.** MOF-5-BPDC was synthesized according to the literature with slight modification.\textsuperscript{1} Zn(NO$_3$)$_2$·6H$_2$O (31 mg), H$_2$BPDC (5 mg) and DEF (16 mL) were charged in a Pyrex vial. The mixture was heated in an 85 °C oven for 24 h to generate the cubic crystals of MOF-5-BPDC. The crystals of MOF-5-BPDC were collected by centrifugation and washed with fresh DMF for 3 times.

**S3.2.5 Synthesis of MOF-177.** MOF-177 was synthesized according to the literature with slight modification.\textsuperscript{6} Zn(NO$_3$)$_2$·6H$_2$O (20 mg), H$_3$BTB (5 mg) and DEF (1 mL) were charged in a Pyrex vial. The mixture was heated in a 100 °C oven for 24 h to generate the crystals of MOF-177. The crystals of MOF-177 were collected by centrifugation and washed with fresh DMF for 3 times.

Figure S20. Microscopic images and PXRD pattern of MOF-177.
**S3.2.6 Synthesis of HKUST-1.** HKUST-1 was synthesized according to the literature with slight modification.\(^7\) 0.49 g Cu(NO\(_3\))\(_2\)·3H\(_2\)O was dissolved in 3 mL of deionized water. 0.24 g H\(_3\)BTC was dissolved in 3 mL of ethanol. The Cu(NO\(_3\))\(_2\) solution was first mixed with 3 mL of DMF in a 20 mL scintillation vial. The H\(_3\)BTC solution and 12 mL of glacial acetic acid were subsequently added to the mixed solution as well. The mixture was heated in a 55 °C oven for 72 h to generate the crystals of HKUST-1.

![Microscopic images and PXRD pattern of HKUST-1](image)

Figure S21. Microscopic images and PXRD pattern of HKUST-1.

**S3.2.7 Synthesis of MOF-1114(Yb).** MOF-1114(Yb) was synthesized according to the literature with slight modification.\(^8\) BDC-NH\(_2\) (13.6 mg, 0.075 mmol), YbCl\(_3\)·6H\(_2\)O (116.5 mg, 0.3 mmol) and nanopure water (0.25 mL) were dissolved in DMF (4.5 mL) in a 20 mL Pyrex vial. The vial was then capped and placed in a 100°C oven for 12 h to yield colorless crystals. After the reaction was cooled down to room temperature, the mother liquor was decanted. The crystals were then washed with fresh DMF (3x) (35 mg, 80%).

![Microscopic images and PXRD pattern of MOF-1114(Yb)](image)

Figure S22. Microscopic images and PXRD pattern of MOF-1114(Yb).
S3.2.8 Synthesis of ZIF-8. ZIF-8 was synthesized according to the literature with slight modification.\(^8\) Zn(NO\(_3\))\(_2\)·4H\(_2\)O (0.210 g, 0.803 mmol) and 2-methylimidazole (H-MeIM) (0.060 g, 0.731 mmol) were dissolved in 18 mL DMF in a 20-mL vial. The vial was then capped and placed in a 140°C oven for 24 h to yield colorless polyhedral crystals. The crystals were then washed with fresh DMF (3x).

![Microscopic images of ZIF-8](image)

Figure S23. Microscopic images of ZIF-8. The brown color in several crystals is possibly due to the decomposition and oxidation of DMF solvents.

S3.3 Synthesis of core MOFs

S3.3.1 Synthesis of UiO-66. UiO-66 single crystals were synthesized according to the literature with slight modification.\(^10\) BDC (5 mg) and ZrOCl\(_2\)·8H\(_2\)O (12 mg) were dissolved in DEF (2 mL) and HAc (2 mL) in a 20 mL Pyrex vial. The vial was then capped and placed in a 135°C oven for 2 d to yield colorless cubic block crystals. After the reaction was cooled down to room temperature, the mother liquor was decanted. The crystals were then washed with fresh DMF (3x) (35 mg, 80%).

![Microscopic images and PXRD pattern of UiO-66](image)

Figure S24. Microscopic images and PXRD pattern of UiO-66.

S3.3.2 Synthesis of UiO-67. UiO-67 single crystals were synthesized according to the literature with slight modification.\(^11\) ZrCl\(_4\) (100 mg), BPDC (100 mg), TFA (2.0 mL)
and DMF (15 mL) were charged in a Pyrex vial. The mixture was heated in 120°C oven for 5 days. After cooling down to room temperature, the resulted single crystals UiO-67 was separated by centrifugation and washed several times with DMF.

S3.3.3 Synthesis of PCN-160. PCN-160 single crystals were synthesized according to the literature with slight modification. ZrCl₄ (200 mg), H₂AZDC (100 mg), trifluoroacetic acid (1.0 mL) and DMF (20 mL) were charged in a Pyrex vial. The mixture was heated in 120 ºC oven for 72 h. After cooling down to room temperature, the red crystals were harvested.

Figure S25. Microscopic and SEM images of PCN-160.

S3.3.4 Synthesis of MOF-808. MOF-808 powders were synthesized according to the literature with slight modification. H₅BTC (210 mg, 1 mmol) and ZrOCl₂·8H₂O (970 mg, 3 mmol) were dissolved in DMF/formic acid (45 mL/45 mL) and placed in a 100 mL screw-capped glass jar, which was heated to 130 °C for two days. A white precipitate was collected by filtration and washed three times with 20 mL of fresh DMF. As-synthesized MOF-808 was then washed by methanol for several times.

Figure S26. PXRD pattern of MOF-808.
S3.3.5 Synthesis of PCN-224. PCN-224(No Metal) was synthesized on the basis of previous reports with slight modifications.\textsuperscript{14} ZrOCl\textsubscript{2} (30 mg), TCPP (10 mg), benzoic acid (600 mg) and DMF (3 mL) were charged in a Pyrex vial. The mixture was heated in a 120 °C oven for 24 h. After cooling down to room temperature, cubic PCN-224 were harvested.

![PCN-224 experimental vs simulated PXRD patterns](image)

Figure S27. PXRD patterns of PCN-224.

S3.3.6 Synthesis of PCN-250(Fe). PCN-250 (Fe) was synthesized on the basis of previous reports with slight modifications.\textsuperscript{15} A mixture of FeCl\textsubscript{3} (500 mg), H\textsubscript{4}ABTC (100 mg), acetic acid (10 mL) and N,N-dimethylformamide (DMF, 20 mL) was charged in a Pyrex vial and heated in a 150°C oven for 24 h. After cooling to room temperature, dark red crystals were collected by centrifugation.

S3.3.7 Synthesis of MIL-125(Ti). MIL-125(Ti) was synthesized on the basis of previous reports with slight modifications.\textsuperscript{11} H\textsubscript{2}BDC (900 mg), methanol (5 mL) and DMF (15 mL) were charged in a Pyrex vial. Ti(OPr)\textsubscript{4} (0.1 mL) was added into the solution slowly. The mixture was heated in 150°C oven overnight. After cooling down to room temperature, the resulted yellow powder was separated by centrifugation and placed in DMF at 70 °C overnight to remove unreacted linker. After washed several times with DMF, the powder was placed in EtOH at 55 °C overnight to remove DMF. The solvent was removed under vacuum at 150°C for 8 h, yielding microporous material.
S3.4 Synthesis of hierarchical MOFs
S3.4.1 Synthesis of PCN-222@MOF-5-NH₂. PCN-222 (10 mg), H₂BDC-NH₂ (10 mg) and DEF (1 mL) were charged in a 4 mL Pyrex vial. The mixture was heated in an 85 °C oven for 24 h resulting in the coordination of BDC-NH₂ to the surface of PCN-222. Zn(NO₃)₂·6H₂O (40 mg) and DEF (1 mL) were further added into the vial. The mixture was heated in a 100 °C oven for 24 h to generate the crystals of PCN-222@MOF-5-NH₂. The crystals of PCN-222@MOF-5-NH₂ were collected by centrifugation and washed with fresh DMF for 3 times.

Figure S28. Microscopic images and PXRD pattern of PCN-222@MOF-5-NH₂.

Figure S29. SEM images of PCN-222@MOF-5-NH₂.
Figure S30. (a, f) Polarized optical image of PCN-222@MOF-5-NH$_2$ crystals placed in between crossed polarizers; (b-e) Optical images of PCN-222@MOF-5-NH$_2$ crystals. It should be noted that the ratio control of core- or shell- MOFs is quite important for the formation of hierarchical structures. As indicated by Figure 1a, increasing the feed ratio of Zr/Zn-MOFs will lead to an increase of Zr-based PCN-222 immobilized inside the Zn-based MOF-5. However, by further increasing the Zr-based core MOF ratio we would eventually reach a “saturated” concentration in comparison to MOF-5, resulting in some uncoated PCN-222 physically mixed in. This problem can be easily avoided by simply lower the feed ratio of PCN-222. We further conducted an experiment with lower PCN-222 to MOF-5 ratio. During the synthesis of PCN-222@MOF-5-NH$_2$, 5 mg PCN-222 (10 mg) instead of 10 mg was added, while other conditions remained same. Only MOF-on-MOF was observed as a product after solvothermal reaction.

**S3.4.2 Synthesis of PCN-222@MOF-5-Br.** PCN-222 (10 mg), H$_2$BDC-Br (10 mg) and DEF (1 mL) were charged in a 4 mL Pyrex vial. The mixture was heated in an 85 ºC oven for 24 h resulting in the coordination of BDC-Br to the surface of PCN-222. Zn(NO$_3$)$_2$·6H$_2$O (40 mg) and DEF (1 mL) were further added into the vial. The mixture was heated in a 100 ºC oven for 24 h to generate the crystals of PCN-222@MOF-5-Br. The crystals of PCN-222@MOF-5-Br were collected by centrifugation and washed with fresh DMF for 3 times.
Figure S31. Microscopic images and PXRD pattern of PCN-222@MOF-5-Br.

Figure S32. SEM images of PCN-222@MOF-5-Br.

**S3.4.3 Synthesis of PCN-222@MOF-5-NDC.** PCN-222 (10 mg), 1,4-H$_2$NDC (10 mg) and DEF (1 mL) were charged in a 4 mL Pyrex vial. The mixture was heated in an 85 °C oven for 24 h resulting in the coordination of 1,4-NDC to the surface of PCN-222. Zn(NO$_3$)$_2$·6H$_2$O (40 mg) and DEF (1 mL) were further added into the vial. The mixture was heated in a 100 °C oven for 24 h to generate the crystals of PCN-222@MOF-5-NDC. The crystals of PCN-222@MOF-5-NDC were collected by centrifugation and washed with fresh DMF for 3 times.

Figure S33. Microscopic images and PXRD pattern of PCN-222@MOF-5-NDC.
S3.4.4 Synthesis of UiO-66@MOF-5. UiO-66 (10 mg), BDC (10 mg) and DEF (1 mL) were charged in a 4 mL Pyrex vial. The mixture was heated in an 80 ºC oven for 24 h resulting in the surface coordination of BDC to UiO-66. Zn(NO$_3$)$_2$·6H$_2$O (40 mg) and DEF (1 mL) were further added into the vial. The mixture was heated in a 100 ºC oven for 24 h to generate the crystals of UiO-66@MOF-5. The crystals of UiO-66@MOF-5 were collected by centrifugation and washed with fresh DMF for 3 times.

Figure S34. Microscopic images and PXRD pattern of UiO-66@MOF-5.

S3.4.5 Synthesis of UiO-67@MOF-5-NH$_2$. UiO-67 (10 mg), H$_2$BDC-NH$_2$ (10 mg) and DEF (1 mL) were charged in a 4 mL Pyrex vial. The mixture was heated in an 80 ºC oven for 24 h resulting in the surface coordination of BDC-NH$_2$ to UiO-67. Zn(NO$_3$)$_2$·6H$_2$O (40 mg) and DEF (1 mL) were further added into the vial. The mixture was heated in a 100 ºC oven for 24 h. The crystals of UiO-67@MOF-5-NH$_2$ were collected by centrifugation and washed with fresh DMF for 3 times.

Figure S35. Microscopic images and PXRD pattern of UiO-67@MOF-5-NH$_2$. 
S3.4.6 Synthesis of PCN-160@MOF-5-NH2. PCN-160 (10 mg), BDC-NH2 (10 mg) and DEF (1 mL) were charged in a 4mL Pyrex vial. The mixture was heated in an 80 °C oven for 24 h resulting in the surface coordination of BDC-NH2 to UiO-67. Zn(NO3)2·6H2O (42 mg, 1.0 mmol) and DEF (1 mL) were further added into the vial. The mixture was heated in a 100 °C oven for 24 h to generate the core-shell crystals of PCN-160@MOF-5-NH2. The crystals of PCN-160@MOF-5-NH2 were collected by centrifugation and washed with fresh DMF for 3 times.

Figure S36. Microscopic images and PXRD pattern of PCN-160@MOF-5-NH2.

Figure S37. SEM images and element mapping of PCN-160@MOF-5-NH2.
The formation of PCN-160@MOF-5-NH$_2$ with surface confined “Janus particle” effect is mainly related to the large size and high density of the PCN-160 single crystal, which allows it to easily precipitate on the bottom of vials, limiting the growth direction, similar to the process in Figure 3c-d. In order to prepare hierarchical MOFs with core-shell or well-mixed distribution, decreasing the size of the core PCN-160 crystals would be helpful to enhance the seed dispersion and achieve the targeted apportionment.

**S3.4.7 Synthesis of PCN-224@MOF-5.** PCN-224 (5 mg), BDC (8.8 mg) and DEF (1 mL) were charged in a Pyrex vial. The mixture was heated in an 85 °C oven for 24 h. Zn(NO$_3$)$_2$·6H$_2$O (40 mg) and DEF (1 mL) were further added into the vial. The mixture was heated in an 85 °C oven for 24 h to generate the crystals of PCN-224@MOF-5. The crystals of PCN-224@MOF-5 were collected by centrifugation and washed with fresh DMF for 3 times.

Figure S39. Microscopic images and PXRD pattern of PCN-224@MOF-5.

Figure S40. SEM images of PCN-224@MOF-5.
**S3.4.8 Synthesis of MOF-808@MOF-5.** MOF-808 (5 mg), BDC (8.8 mg) and DEF (1 mL) were charged in a 4mL Pyrex vial. The mixture was heated in an 80 °C oven for 24 h resulting in the surface coordination of BDC to MOF-808. Zn(NO₃)₂·6H₂O (40 mg) and DEF (1mL) were further added into the vial. The mixture was heated in a 100 °C oven for 24 h to generate the crystals of MOF-808@MOF-5. The crystals of MOF-808@MOF-5 were collected by centrifugation and washed with fresh DMF for 3 times.

![Microscopic images and PXRD pattern of MOF-808@MOF-5.](image)

**Figure S41.** Microscopic images and PXRD pattern of MOF-808@MOF-5.

**S3.4.9 Synthesis of PCN-250(Fe)@MOF-5-NH₂.** PCN-250(Fe) (5 mg), BDC-NH₂ (10 mg) and DEF (1 mL) were charged in a 4 mL Pyrex vial. The mixture was heated in an 80 °C oven for 24 h resulting in the surface coordination of BDC-NH₂ to PCN-250(Fe). Zn(NO₃)₂·6H₂O (42 mg) and DEF (1mL) were further added into the vial. The mixture was heated in a 100 °C oven for 24 h to generate the core-shell crystals of PCN-250(Fe)@MOF-5-NH₂. The crystals were collected by centrifugation and washed with fresh DMF for 3 times.

![Microscopic images and PXRD pattern of PCN-250(Fe)@MOF-5-NH₂.](image)

**Figure S42.** Microscopic images and PXRD pattern of PCN-250(Fe)@MOF-5-NH₂.
S3.4.10 Synthesis of PCN-222@MOF-177. PCN-222 (5 mg), H$_3$BTB (10 mg) and DEF (1 mL) were charged in a 4 mL Pyrex vial. The mixture was heated in an 80 ºC oven for 24 h resulting in the surface coordination of BTB to PCN-222. Zn(NO$_3$)$_2$·6H$_2$O (40 mg) and DEF (1mL) were further added into the vial. The mixture was heated in a 100 ºC oven for 24 h to generate the crystals of PCN-222@MOF-177. The crystals were collected by centrifugation and washed with fresh DMF for 3 times.

Figure S43. Microscopic images and PXRD pattern of PCN-222@MOF-177.
S3.4.11 Synthesis of MIL-125(Ti)@MOF-5-NH$_2$. MIL-125(Ti) (5 mg), H$_2$BDC-NH$_2$ (10 mg) and DEF (1 mL) were charged in a 4 mL Pyrex vial. The mixture was heated in an 80 ºC oven for 24 h resulting in the surface coordination of BDC-NH$_2$ to MIL-125(Ti). Zn(NO$_3$)$_2$·6H$_2$O (40 mg) and DEF (1 mL) were further added into the vial. The mixture was heated in a 100 ºC oven for 24 h to generate the crystals of MIL-125(Ti)@MOF-5-NH$_2$. The crystals were collected by centrifugation and washed with fresh DMF for 3 times.

![Microscopic images and PXRD pattern of MIL-125@MOF-5-NH$_2$.](image)

Figure S44. Microscopic images and PXRD pattern of MIL-125@MOF-5-NH$_2$. 

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S3.4.12 Synthesis of PCN-222@HKUST-1. PCN-222 (5 mg), H₃BTC (24 mg), EtOH (0.3 mL) and DMF (0.3 mL) were charged in a 4 mL Pyrex vial. The mixture was heated in a 55°C oven for 24 h resulting in the surface coordination of BTC to PCN-222. Cu(NO₃)₂·3H₂O (49 mg), H₂O (0.3 mL) and HAc (1.2 mL) were further added into the vial. The mixture was heated in a 55 ºC oven for 3 d to generate the crystals of PCN-222@HKUST-1. The crystals were collected by centrifugation and washed with fresh DMF for 3 times.

Figure S45. Microscopic images and PXRD pattern of PCN-222@HKUST-1.
S3.4.13 Synthesis of PCN-222@MOF-1114. PCN-222 (5 mg), H$_2$BDC-NH$_2$ (13.6 mg), and DMF (2 mL) were charged in a Pyrex vial. The mixture was heated in an 85ºC oven for 24 h. YbCl$_3$·6H$_2$O (116 mg), H$_2$O (0.25 mL) and DMF (2.5 mL) were further added into the vial. The mixture was heated in a 100 ºC oven for 12 h to generate the crystals of PCN-222@MOF-1114. The crystals were collected by centrifugation and washed with fresh DMF for 3 times.

Figure S46. Microscopic images and PXRD pattern of PCN-222@MOF-1114.
S3.4.14 Synthesis of PCN-224@HKUST-1. PCN-224 (5 mg), H$_3$BTC (24 mg), EtOH (0.3 mL) and DMF (0.3 mL) were charged in a 4 mL Pyrex vial. The mixture was heated in a 55ºC oven for 24 h resulting in the surface coordination of BTC to PCN-222. Cu(NO$_3$)$_2$·3H$_2$O (49 mg), H$_2$O (0.3 mL) and HAc (1.2 mL) were further added into the vial. The mixture was heated in a 55 ºC oven for 3 d to generate the crystals of PCN-224@HKUST-1. The crystals were collected by centrifugation and washed with fresh DMF for 3 times.

Figure S47. Microscopic images and PXRD pattern of PCN-224@HKUST-1.
**S3.4.15 Synthesis of HKUST-1@MOF-5.** HKUST-1 (5 mg), H$_2$BDC (10 mg) and DEF (1 mL) were charged in a 4 mL Pyrex vial. The mixture was heated in an 80 °C oven for 24 h resulting in the surface coordination of BDC to HKUST-1. Zn(NO$_3$)$_2$·6H$_2$O (42 mg) and DEF (1 mL) were further added into the vial. The mixture was heated in a 100 °C oven for 24 h to generate the core-shell crystals of HKUST-1@MOF-5. The crystals were collected by centrifugation and washed with fresh DMF for 3 times.

Figure S48. Microscopic images and PXRD pattern of HKUST-1@MOF-5.
S3.4.16 Synthesis of UiO-66@HKUST-1. UiO-66 (5 mg), H$_3$BTC (24 mg), EtOH (0.3 mL) and DMF (0.3 mL) were charged in a 4 mL Pyrex vial. The mixture was heated in a 55ºC oven for 24 h resulting in the surface coordination of BTC to PCN-222. Cu(NO$_3$)$_2$·3H$_2$O (49 mg), H$_2$O (0.3 mL) and HAc (1.2 mL) were further added into the vial. The mixture was heated in a 55 ºC oven for 3 d to generate the crystals of UiO-66@HKUST-1. The crystals were collected by centrifugation and washed with fresh DMF for 3 times.

Figure S49. Microscopic images and PXRD pattern of UiO-66@HKUST-1.
S3.4.17 Synthesis of PCN-222@ZIF-8. PCN-222 (5 mg), 2-methylimidazole (H-mIM) (18 mg) and DMF (2.7 mL) were charged in a Pyrex vial. The mixture was heated in a 100°C oven for 24 h. Zn(NO$_3$)$_2$·4H$_2$O (63 mg) and DMF (2.7 mL) were further added into the vial. The mixture was heated in a 120 °C oven for 48 h to generate the crystals of PCN-222@ZIF-8. The crystals were collected by centrifugation and washed with fresh DMF for 3 times.

Figure S50. Microscopic images of PCN-222@ZIF-8.

Figure S51. PXRD pattern of PCN-222@ZIF-8.
S3.4.18 Synthesis of TCPP@ZIF-8. TCPP (5 mg), 2-methylimidazole (H-mIM) (18 mg), Zn(NO$_3$)$_2$$\cdot$4H$_2$O (63 mg) and DMF (5.4 mL) were charged in a Pyrex vial. The mixture was heated in a 120 °C oven for 48 h. The obtained powder TCPP@ZIF-8 were collected by centrifugation and washed with fresh DMF for 3 times.

Figure S52. SEM images of one-pot synthesized TCPP@ZIF-8 (a) and comparison of traditional one-pot synthesis (b) and controlled stepwise synthesis reported in this work (c). In the homogenous nucleation conditions (Zn$^{2+}$, TCPP linker and mIM linker), there exists competitive coordination between TCPP and mIM, which will interfere with ZIF-8 growth process and induce impurity problems. Under this synthetic condition, the crystallinity of ZIF-8 is low as indicated by the SEM images, and porphyrin functionalities (TCPP) are weakly immobilized due to weak Zn-O bonds. However, in the heterogenous nucleation conditions (Zn$^{2+}$, mIM linker and functionalized PCN-222), there exist no competitive coordination since only Zn$^{2+}$ and mIM linker are dissolved in the solution. During this controlled stepwise synthesis, functional groups can be introduced without interfering with the ZIF-8 growth. Highly crystalline and pure MOF crystals are obtained and no impurity was observed as indicated by PXRD patterns. Moreover, the strongly immobilized TCPP in PCN-222@ZIF-8, due to robust Zr-O bonds, can also be utilized for targeted applications that require harsh conditions.
S4. Porosity and Thermal Stability

S4.1 N\textsubscript{2} sorption isotherm.

Figure S53. N\textsubscript{2} sorption isotherms and corresponding pore size distributions of MOF-5 (a,c) and HKUST-1 (b,d) calculated by density functional theory (DFT) method.
Figure S54. N\textsubscript{2} sorption isotherms and corresponding pore size distributions of PCN-224 (a,c) and PCN-222 (b,d) calculated by density functional theory (DFT) method.
Figure S55. N₂ sorption isotherms and corresponding pore size distributions of PCN-222@MOF-5-(8%, a,c) and -(14%, b,d) calculated by density functional theory (DFT) method.
Figure S56. N$_2$ sorption isotherms and corresponding pore size distributions of PCN-222@HKUST-1 (a,c) and PCN-224@HKUST-1 (b,d) calculated by density functional theory (DFT) method.

Figure S57. (a) N$_2$ sorption isotherms of PCN-222, HKUST-1 and PCN-222@HKUST-1; (b) N$_2$ sorption isotherms of PCN-224, HKUST-1 and PCN-224@HKUST-1; and (c) PXRD patterns of PCN-222, PCN-224, HKUST-1, PCN-222@HKUST-1 and PCN-224@HKUST-1.
Table S3. Pore features of MOF-5, PCN-222@MOF-5-(8%, 14%) and PCN-222.

| Entry | Samples             | \(S_{\text{BET}}^a\) (m\(^2\)g\(^{-1}\)) | \(V_t^b\) (cm\(^3\)g\(^{-1}\)) |
|-------|---------------------|---------------------------------------|---------------------------------|
| 1     | MOF-5               | 3418                                  | 1.27                            |
| 2     | PCN-222@MOF-5-(8%) | 3310                                  | 1.29                            |
| 3     | PCN-222@MOF-5-(14%)| 3249                                  | 1.32                            |
| 4     | PCN-222             | 2208                                  | 1.48                            |

\(S_{\text{BET}}^a\): Brunauer-Emmett-Teller (BET) specific surface area; \(V_t^b\): total specific pore volume determined by using the adsorption branch of the N\(_2\) isotherm at \(P/P_0 = 0.95\). For comparison, as the PCN-222 ratio increases in the hierarchical composites, the BET surface area of hierarchical MOFs decreases while the total pore volume increases.

S4.2 Thermal gravimetric analysis.

![Graph showing thermogravimetric analysis (TGA) of MOF-5 and PCN-224@MOF-5.](figure_s58)

Figure S58. Thermogravimetric analysis (TGA) of MOF-5 and PCN-224@MOF-5.
Figure S59. Thermogravimetric analysis (TGA) of PCN-222@MOF-5-(8%) and PCN-222@MOF-5-(14%).
S5. Chemical Stability Test

Figure S60. Optical microscopy images of the stepwise decomposition of MOF-5 crystals during treatment with an aqueous HCl solution (pH = 1). Before the addition of the HCl solution, the MOF-5 crystals were colorless and transparent (a). Since Zn-based MOF-5 are acid-sensitive, after acid addition the crystals quickly dissolved from outside to the inside and released white BDC linkers as a decomposition product (due to the low solubility of BDC in HCl at room temperature). Photos at various time periods after the acid addition including 5 s (b), 10 s (c), 15 s (d), 20 s (e), 25 s (f) and 30 s (g) were recorded. After 30 s, the acid solution was removed and replaced by a drop of DMF to dissolve the decomposed BDC on the MOF surface. Photos at various time periods after the DMF addition including 10 s (h) and 20 s (i) were recorded.
Figure S61. Optical microscopy images of the stepwise decomposition of MOF-5 crystals during treatment with acetic acid. Before the addition of acetic acid, the MOF-5 crystals were colorless and transparent (a). Since the Zn-based MOF-5 is acid-sensitive, after acid addition the crystals quickly dissolved from the outside to the inside, releasing white BDC linker as a decomposition product (due to the low solubility of BDC in acetic acid at room temperature). Photos at various time periods after acid addition, 5 s (b), 10 s (c), 15 s (d), 20 s (e) and 25 s (f) were recorded. After 25 s, the acid solution was removed and replaced by a drop of DMF to dissolve the decomposed BDC on the MOF surface. Photos were taken at various time periods after DMF addition: 5 s (g), 10 s (h) and 20 s (i) were recorded.
Figure S62. Optical microscopy images of PCN-222 single crystals under the treatment of acetic acid, indicating the high chemical stability of Zr-based PCN-222. Before the addition of acetic acid, the PCN-222 crystals displayed a purple needle-like morphology (a). Since the Zr-based PCN-222 is acid-stable, after acid addition, the crystals maintained a needle morphology. The porphyrin TCPP linkers were protonated after acid addition and exhibited a green color (b). After 1 min, the acetic acid was fully volatilized, leading to the formation of the purple needle-like PCN-222 as a dry sample (c).
Figure S63. Optical microscopy images of PCN-224(Zn)@MOF-5 single crystals treated with acetic acid, indicating that PCN-224(Zn) crystals were located throughout the MOF-5 crystals. Taking advantages of the high chemical stability of the Zr-based PCN-224(Zn) and the labile nature of Zn-MOF-5, we were able to monitor the stepwise dissolution of MOF-5 under acidic treatment and track the release of immobilized PCN-224(Zn) such that the approximate distribution of PCN-224(Zn) can be obtained. Before the addition of acetic acid, PCN-224(Zn)@MOF-5 crystals displayed a hierarchical structure with small cubic PCN-224(Zn) crystals immobilized in a large cubic MOF-5 crystal (a). Since the Zr-based PCN-224(Zn) is acid-stable, after the acid addition, the shell MOF-5 gradually dissolved and BDC linkers were released, while the core crystals of PCN-224(Zn) remained. Photos at various time periods after the acid addition: 5 s (b), 20 s (c) and 40 s (d) were recorded. The release of PCN-224(Zn) was observed, indicating the presence of PCN-224(Zn) on the surface of the hierarchical MOFs (c). Further treating the crystals with acid solutions in DMF results in a continuous dissolution of MOF-5 and a release of PCN-224(Zn) crystals, with photos recorded at 60 s (e), 80 s (f), 100 s (g-h), 120 s (i) and 140 s (j), confirming that PCN-224(Zn) crystals were located throughout the MOF-5 crystals. (d) insert figure and (g) are the corresponding figures of (d) and (h) except that the samples have been exposed to white light to better present the distribution of PCN-224(Zn) in the hierarchical PCN-224(Zn)@MOF-5.
S6. Size Selective Biomimetic Catalysis

S6.1 Synthesis of PCN-222(Fe). ZrCl₄ (70 mg), FeTCCPCl (50 mg) and benzoic acid (2400 mg) in N,N-diethylformamide (8 mL) were ultrasonically dissolved in a 20 mL Pyrex vial. The mixture was heated at 120 °C in an oven for 48 h. After cooling down to room temperature, microcrystals were harvested by filtration.

S6.2 Synthesis of PCN-222(Fe)@ZIF-8. PCN-222(Fe) (5 mg), 2-methylimidazole (H-mIM) (18 mg) and methanol (1.5 mL) were charged in a Pyrex vial. The mixture was placed at room temperature for 24 h. Zn(NO₃)₂·4H₂O (32 mg) and methanol (1.5 mL) were further added into the vial. The mixture was placed under room temperature for 48 h to generate PCN-222(Fe)@ZIF-8. The composites were collected by centrifugation and washed with fresh DMF for 3 times.

S6.3 Size Selective Biomimetic Catalysis. The size selective catalysis was carried out on the basis of previous reports with slight modifications. FeTCCPP can catalyze the oxidation of o-phenylenediamine (o-PDA) and 2-2'-azo-bis(3-ethylbenzthiazoline-6-sulfonic acid) (ABTS) in the presence of H₂O₂. The products were confirmed by scanning the UV-vis absorbance on spectrophotometer and the concentrations of products were calculated by their molar extinction coefficients at respective wavelengths (16300 M⁻¹cm⁻¹ at 450 nm for the peroxidized product of o-PDA and 3.6×10⁴ M⁻¹cm⁻¹ at 418 nm for peroxidized product of ABTS). The concentration of H₂O₂ was determined spectrophotometrically at 240 nm with ε = 43.6 M⁻¹cm⁻¹. Kinetic measurements were carried out in time course mode by monitoring the absorbance change at 450 nm for o-PDA and 418 nm for ABTS. The Michaelis-Menten equation was used for enzyme kinetics.

\[ V_0 = \frac{V_{max}[S]}{K_m + [S]} \]

V₀ is the initial catalytic rate, V_max is the maximum reaction rate, which is obtained when the catalytic sites on the enzyme are saturated with substrate. [S] is the substrate concentration and K_m is the apparent Michaelis-Menten constant. Lineweaver-Burk plot was employed for illustrating kinetic data and calculate the parameters by taking the reciprocal of both sides of the Michaelis–Menten equation.

The reactions were conducted in the 3ml cuvette directly. Before incorporation, MOF samples were activated by solvent exchange with DMF and dichloromethane for three times and further dried overnight at 70 °C under vacuum. The substrate (1 mL) and 1 mg MOF catalyst were added to buffer followed with the addition of H₂O₂ (1 mL). After a quick shaking, the cuvette was put in the UV sample holder as quickly as possible. The data were collected using the kinetic mode and the plots of absorbance to time were obtained. The background needs to be scanned before data collection with addition of water instead of H₂O₂. The specific activities were calculated by comparing
the reaction rate catalyzed by each catalyst.

Figure S64. The initial o-PDA oxidation profile catalyzed by PCN-222(Fe) (a) and PCN-222(Fe)@ZIF-8 (c). The concentrations of H$_2$O$_2$ range from 2.5 mM to 20 mM. Lineweaver-Burk plot of o-PDA oxidation catalyzed by PCN-222(Fe) (b) and PCN-222(Fe)@ZIF-8 (d).
Figure S65. The initial ABTS oxidation profile catalyzed by PCN-222(Fe) (a) and PCN-222(Fe)@ZIF-8 (c). The concentrations of H_2O_2 range from 0.2 mM to 2 mM. (b) Lineweaver-Burk plot of ABTS oxidation catalyzed by PCN-222(Fe). (d) Relative activity of PCN-222(Fe) and hierarchical PCN-222(Fe)@ZIF-8 for the oxidation of o-phenylenediamine (o-PDA) and ABTS.

Table S4. Comparison of kinetic parameters for PCN-222(Fe) and hierarchical PCN-222(Fe)@ZIF-8.

| Catalyst              | Substrate | K_m (mM) | k_cat (min) | k_cat/K_m | V_max (mM/min) |
|-----------------------|-----------|----------|-------------|-----------|----------------|
| PCN-222(Fe)           | o-PDA     | 7.27     | 2.98        | 0.410     | 0.00149        |
| PCN-222(Fe)@ZIF-8     | o-PDA     | 0.996    | 0.27        | 0.271     | 0.000135       |
| PCN-222(Fe)           | ABTS      | 9.47     | 85.4        | 9.02      | 0.0427         |
| PCN-222(Fe)@ZIF-8     | ABTS      | -        | -           | -         | -              |

S7. Photo-triggered Guest Release

S7.1 Photothermal effect of porphyrinic MOFs. The photothermal experiments were carried out on the basis of previous reports with slight modifications. Typically, 20 mg of activated MOFs were immersed in 10 mL H_2O under the irradiation of LED lamps (λ = 410 nm, 150 W) for 30 mins. The initial temperature of water and the
ambient temperature is $22.0 \, ^\circ C$. For MOF-177 sample, ethanol used as solvents instead of water because MOF-177 is water sensitive and gradually decomposes under aqueous solution. After exposure, final temperatures were recorded in Table S5.

**Table S5.** The measured temperature of solution with MOFs in water at ambient temperature ($22.0 \, ^\circ C$) under visible light irradiation.$^a$

| Entry | MOFs               | Time (min) | Temperature ($^\circ C$) |
|-------|--------------------|------------|--------------------------|
| 1     | No catalyst        | 30         | $22.0 - 22.1$            |
| 2     | PCN-223            | 30         | $22.0 - 28.6$            |
| 3     | ZIF-8              | 30         | $22.0 - 22.2$            |
| 4     | MOF-177$^b$        | 30         | $22.0 - 22.1$            |
| 5     | PCN-223@ZIF-8      | 30         | $22.0 - 26.1$            |
| 6     | PCN-223@MOF-177$^b$| 30         | $22.0 - 26.3$            |

$^a$Conditions: 20 mg of MOFs, 10 mL H$_2$O, visible light ($\lambda = 410 \, \text{nm}, 150 \, \text{W}$), the initial temperature of water and the ambient temperature is $22.0 \, ^\circ C$. $^b$Ethanol used as solvents instead of water.

**S7.2 Incorporation of anthracene/4-nitrophenol into MOFs.** The guest adsorption experiments were carried out on the basis of previous reports with slight modifications.$^{18}$ PCN-223 was prepared on the basis of previous reports without modifications.$^{19}$ The guest incorporation within the pores of MOF-177, ZIF-8, PCN-223 and their hierarchical structures were first studied. Before incorporation, MOF samples were activated by solvent exchange with DMF and dichloromethane three times and further dried overnight at $70 \, ^\circ C$ under vacuum. The guest loadings were then performed by soaking 10 mg of activated MOFs (PCN-223, ZIF-8, MOF-177, and the hierarchical PCN-223@MOF-177, PCN-223@ZIF-8) in a 20 mM cyclohexane solution of anthracene (or 20 mM 4-nitrophenol, 2 mL) in a thermomixer at room temperature for 24 h. For physical mixtures of PCN-223 and MOF-177, about 2 mg of PCN-223 and about 8 mg of MOF-177 were mixed together. After insertion of the guest, the MOF samples were washed by fresh cyclohexane for several times to remove the guest molecules from the surface of the crystals until there is no remaining anthracene (or 4-nitrophenol) in the supernatant confirmed by UV-vis spectroscopy. The loading of anthracene (or 4-nitrophenol) in various MOF samples was calculated by the comparison of the UV-vis absorbance (anthracene at $\lambda = 355 \, \text{nm}$, 4-nitrophenol at $\lambda = 282 \, \text{nm}$).
Table S6. Guest loading amounts in various porous MOF samples.

| Guest       | MOFs          | Loading Amount (mg/g) |
|-------------|---------------|-----------------------|
| Anthracene  | ZIF-8         | 34.2                  |
| Anthracene  | PCN-223       | 9.5                   |
| Anthracene  | PCN-223@ZIF-8 | 24.3                  |
| 4-Nitrophenol | ZIF-8       | 90.4                  |
| 4-Nitrophenol | MOF-177    | 162                   |
| 4-Nitrophenol | PCN-223     | 62.3                  |
| 4-Nitrophenol | PCN-223@ZIF-8 | 81.0                  |
| 4-Nitrophenol | PCN-223@MOF-177 | 154                  |
| 4-Nitrophenol | Physical mixtures of PCN-223 and MOF-177 | 148                  |

S7.3 **Photo-triggered guest release.** The photo-triggered release was carried out on the basis of previous reports with slight modifications. 18 Release experiments were conducted by using an LED light source with an emission wavelength at 410 nm and the release amounts of the guest molecules were further analyzed by UV-Vis spectroscopy. 10 mg of guest loaded MOFs were dispersed into 1 mL of cyclohexane. The sample was then directly irradiated with the LED lamp (150 W, \( \lambda = 410 \) nm) for various periods (0 - 5 h). After each experiment, samples were centrifuged, and the UV-Vis spectra of the supernatants with and without lamp irradiation were recorded and compared to each other. Reference experiments were performed with only shell or core MOFs for guest release. The release amount can be calculated from the standard curve (anthracene at \( \lambda = 355 \) nm, 4-nitrophenol at \( \lambda = 282 \) nm).
Figure S66. UV-Vis spectra of 4-nitrophenol released from PCN-223@MOF-177 as a function of time with lamp irradiation (a) and without lamp irradiation (b).

Figure S67. 4-nitrophenol release from hierarchical PCN-223@ZIF-8 as a function of time with and without lamp irradiation. Hierarchical PCN-223@ZIF-8 and PCN-223@MOF-177 can achieve more efficient photo-triggered release than its single component or physical mixtures. The data were collected using the kinetic mode and the plots of absorbance to time were obtained.
Figure S68. UV-Vis spectra of anthracene released from PCN-223@ZIF-8 as a function of time with lamp irradiation (a) and without lamp irradiation (c). For comparison, UV-Vis spectra of anthracene released from ZIF-8 as a function of time with lamp irradiation (b) was also included.

Figure S69. Anthracene release from hierarchical PCN-223@ZIF-8 as a function of time with and without lamp irradiation.
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