Supporting Information

A Robust Hollow Metal-Organic Framework with Enhanced Diffusion for Size Selective Catalysis

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Section S1. Materials

Zirconium(IV) chloride (ZrCl₄, Alfa Aesar, 98%), 1,4-dicarboxybenzene (H₂BDC, Aladdin, 99%), fumaric acid (FA, J&K, 98%), acetic acid glacial (HOAC, Greagent, 99.5%), formic acid (HCOOH, Alfa Aesar, 98%), concentrated Hydrochloric acid (HCl, SCR, AR), sulfuric acid (H₂SO₄, SCR, AR), n-dodecane (C₁₂H₂₆, Macklin, 99%), nitrobenzene (NB, Macklin, 99%), 1-nitronaphthalene (NN, J&K, 98%), ethanethiol (J&K, 98%), 1-adamantanethiol (C₁₀H₁₆S, Bide, 95%), n-decane (C₁₀H₂₂, Aladdin, 98%), chloroplatinic acid hexahydrate (H₂PtCl₆·6H₂O, Macklin, AR, Pt>37.5%), tetramethylammonium bromide (TMABr, Alfa Aesar, 98%), polyvinylpyrrolidone (PVP, Alfa Aesar, M.W. 24000), ethylene glycol (EG, Greagent, 99.5%), aniline (C₆H₇N, Adamas, 99%), 1-aminonaphthalene (C₁₀H₈N, Adamas, 99%), 3 Å molecular sieves (3MS, K₆Na₁₂.)
\[n[(\text{AlO}_2)_{12}(\text{SiO}_2)_{12}] \times \text{H}_2\text{O}, \text{ Aladdin}], 4\text{-ethynyltoluene } (\text{C}_9\text{H}_8, \text{ Macklin}, 98\%), 1\text{-ethynlnaphthalene } (\text{C}_{12}\text{H}_8, \text{ Aladdin}, 97\%), \text{ gold chloride solution } (\text{HAuCl}_4, \text{ Aladdin, Au} \geq 47.5\%), \text{ dichloromethane } (\text{CH}_2\text{Cl}_2, \text{ Greagent, 99.8\%}), 1,4\text{-dioxane } (\text{C}_4\text{H}_8\text{O}_2, \text{ Collins, 99.7\%}), \text{ dimethyl sulfoxide-D}_6 \ (\text{DMSO-D}_6, \text{ Adamas, 99.9\%}), \text{ trisodium citrate } (\text{Na}_3\text{C}_6\text{H}_5\text{O}_7, \text{ Fisher Scientific, 99\%}), \text{ n-hexane } (\text{C}_6\text{H}_{14}, \text{ Aladdin, 98\%}), \text{ toluene } (\text{Greagent, 99.5\%}), \text{ acetone } (\text{Greagent, 99.5\%}), \text{ N,N-dimethylformamide } (\text{DMF, Greagent, 99.5\%}), \text{ ethanol } (\text{Greagent, 99.7\%}), \text{ and anhydrous methanol } (\text{Greagent, 99.5\%}) \text{ were purchased from the mentioned sources and used without further purification.}

**Section S2. Synthesis**

**Synthesis of UiO-66**

UiO-66 was synthesized by dissolving $\text{ZrCl}_4$ (174.78 mg, 0.75 mmol) and $\text{H}_2\text{BDC}$ (124.59 mg, 0.75 mmol) in 30 mL DMF and 4.0 mL acetic acid. The mixture was heated in an oven at 120 °C for 20 h. After cooling down to room temperature, the product was collected by centrifugation and washed by fresh DMF and anhydrous methanol three times, respectively.

**Synthesis of UiO-66@MOF-801 with different UiO-66/MOF-801 growth solution ratio**

2.5 mg as-synthesized UiO-66 was dispersed in DMF which contains different amount $\text{ZrCl}_4$ and fumaric acid according to the table below. The suspension was stirred for 5 min. After mixing, 184 eq. $\text{HCOOH}$ (with respect to FA) was added. The mixture was heated in an oven at 120 °C for 2 h. After cooling down to room temperature, the product was collected by centrifugation and
washed by fresh DMF and anhydrous methanol three times, respectively. The amount of ZrCl$_4$, FA and HCOOH for UiO-66/MOF-801 growth solution ratio are detailed below:

| The UiO-66/MOF-801 growth solution ratio | $V_{30\text{mM} \text{ZrCl}_4}$ (mL) | $V_{30\text{mM} \text{FA}}$ (mL) | $V_{\text{HCOOH}}$ (µL) |
|-----------------------------------------|---------------------------------|-----------------|-----------------|
| 1 : 2.5                                 | 0.125                           | 0.125           | 26              |
| 1 : 5                                   | 0.25                            | 0.25            | 52              |
| 1 : 10                                  | 0.5                             | 0.5             | 104             |
| 1 : 15                                  | 1                               | 1               | 208             |

**Synthesis of UiO-66@MOF-801 with different amounts of HCOOH**

To a FA solution in DMF (0.5 mL, 30 mM) was added 2.5 mg of as-synthesized UiO-66 under sonication. After mixing, a ZrCl$_4$ solution in DMF (0.5 mL, 30 mM) was added and stirred for 10 min. Then, 92–368 eq. (52/104/156/208 µL) HCOOH (with respect to FA) was added in to the solution. The mixture was heated in an oven at 120 ºC for 2 h. After cooling down to room temperature, the product was collected by centrifugation and washed by fresh DMF and anhydrous methanol three times, respectively.

**Synthesis of UiO-66@MOF-801 with different reaction time**

To a FA solution in DMF (0.5 mL, 30 mM) was added 2.5 mg of as-synthesized UiO-66 under sonication. After mixing, a ZrCl$_4$ solution in DMF (0.5 mL, 30 mM) was added and stirred for 10 min. Then, 52 µL HCOOH was added into the solution. The mixture was heated in an oven at 120 ºC for different time (0/30/60/120 min). After cooling down to room temperature, the product was
collected by centrifugation and washed by fresh DMF and anhydrous methanol three times, respectively.

**Etching UiO-66@MOF-801 with HCOOH**

The as-synthesized UiO-66@MOF-801 (92 eq. HCOOH, the UiO-66/MOF-801 growth solution ratio is 1:10, 120 min) was re-dispersed in 1.25 mL DMF containing 260 µL HCOOH under sonication. After mixing, the mixture was heated in an oven at 120 ºC for 4 h.

**Synthesis of hollow MOF-801**

The as-synthesized UiO-66@MOF-801 (92 eq. HCOOH, the UiO-66/MOF-801 growth solution ratio is 1:10, 120 min) was re-dispersed in 1.25 mL DMF containing 0.038 mmol FA (4.4 mg) and 260 µL HCOOH under sonication. After mixing, the mixture was heated in an oven at 120 ºC for 4 h. After cooling down to room temperature, the product was collected by centrifugation and washed by fresh DMF and anhydrous methanol three times, respectively.

**Synthesis of MOF-801**

MOF-801 was synthesized by dissolving ZrCl$_4$ (481.93 mg, 2.1 mmol) and FA (719.6 mg, 6.2 mmol) in 80 mL DMF. After mixing, 5.46 mL HCOOH was added. The mixture was heated in an oven at 120 ºC for 24 h. After cooling down to room temperature, the product was collected by centrifugation and washed by fresh DMF and anhydrous methanol three times, respectively.

**Synthesis of 3 nm Pt nanoparticles (NPs)**
Pt NPs were synthesized according to the reported method. \(^2\) Firstly, dissolving PVP (277.85 mg) and H\(_2\)PtCl\(_6\)·6H\(_2\)O (64.75 mg) in 21.25 mL EG. Then, the mixture was heated to 200 °C in an oil bath under a nitrogen atmosphere with magnetic stirring (350 rpm). When the color of solution changes into black, 3.75 mL 0.5 M TMABr EG solution was added into the mixture to continue stirring 20 min. After cooling down to room temperature, acetone (90 mL) was then added to form a cloudy black suspension, which was separated by centrifugation. The black product was collected by discarding the colorless supernatant. The products were further washed three times by precipitation/dissolution (redispersed in 20 mL of ethanol and then precipitated by adding 80 mL of hexanes). The nanocrystals were then redispersed in 25 mL of DMF for later use.

**Synthesis of Pt⊂MOF-801** \(^3\)

Pt⊂MOF-801 was synthesized by dissolving ZrCl\(_4\) (174.78 mg, 0.75 mmol) and FA (124.59 mg, 1.07 mmol) in 30 mL DMF. After mixing, 4.0 mL acetic acid and 6 mg as-synthesized Pt NPs were added. Then, the mixture was heated in an oven at 120 °C for 20 h. After cooling down to room temperature, the product was collected by centrifugation and washed by fresh DMF and anhydrous methanol three times, respectively.

**Synthesis of Pt⊂UiO-66** \(^3\)

Pt⊂UiO-66 was synthesized by dissolving ZrCl\(_4\) (174.78 mg, 0.75 mmol) and H\(_2\)BDC (124.59 mg, 0.75 mmol) in 30 mL DMF. After mixing, 4.0 mL acetic acid and 6 mg as-synthesized Pt NPs were added. Then, the mixture was heated in an oven at 120 °C for 20 h. After cooling down to room temperature, the product was collected by centrifugation and washed by fresh DMF and anhydrous methanol three times, respectively.
Synthesis of Pt⊂UiO-66@MOF-801

2.5 mg of as-synthesized Pt⊂UiO-66 was added to a FA solution in DMF (0.5 mL, 30 mM) under sonication. After mixing, a ZrCl₄ solution in DMF (0.5 mL, 30 mM) was added and stirred for 10 min. Then, 52 µL HCOOH was added to the solution. The mixture was heated in an oven at 120 °C for 2 h. After cooling down to room temperature, the product was collected by centrifugation and washed by fresh DMF and anhydrous methanol three times, respectively.

Synthesis of Pt⊂hollow MOF-801

The as-synthesized Pt⊂UiO-66@MOF-801 was re-dispersed in 1.25 mL DMF containing 0.038 mmol FA (4.4 mg) and 260 µL HCOOH under sonication. After mixing, the mixture was heated in an oven at 120 °C for 4 h. After cooling down to room temperature, the product was collected by centrifugation and washed by fresh DMF and anhydrous methanol three times, respectively.

Synthesis of PVP-stabilized 13 nm Au nanoparticles (NPs)

13 nm Au nanoparticles (NPs) were prepared by a sodium citrate reduction method of HAuCl₄. An aqueous solution of HAuCl₄ (0.01%, 150 ml) was brought to a vigorous boil with rapid stirring in a 250 mL round bottom flask fitted with a reflux condenser. When the solution started to boil, an aqueous solution of trisodium citrate (1%, 4.5 ml) was added. The mixture was refluxed with stirring for another 20 minutes. The resulting deep red suspension and was then removed from the heat. After the Au NP sol was cooled to room temperature, a solution of PVP (0.5 g) in water (20 ml) was added dropwise to the Au NP sol with stirring, and the mixture was further stirred at room temperature for 24 hours. The Au NPs were collected by centrifugation at 14,000 rpm for 30 minutes, washed by anhydrous methanol three times.
Synthesis of Au⊂MOF-801/Au⊂UiO-66

The Au⊂MOF-801/Au⊂UiO-66 was prepared using a reported method. Firstly, MOF-801 were activated under vacuum in an 80 °C oven overnight. 5 mg MOF-801/UiO-66 was sonicated and stirred in a solution containing 500 µL ethanol and 2.5 µL aqueous solution of HAuCl₄ (10 wt %). Then 500 µL CH₂Cl₂ was added to the mixture. The mixture was then dropwise added to n-hexane. The slow settlement of particles in the solution should be observed. Particles were collected by centrifugation and wash twice with n-hexane. The product was activated under vacuum in an 80 °C oven overnight. Then the obtained powder was placed in an autoclave and reduced under a pure H₂ atmosphere at 200 °C for 30 min. The final product was sonicated in methanol and soaked in methanol.

Synthesis of Au⊂UiO-66@MOF-801

To a FA solution in DMF (0.5 mL, 30 mM) was added 2.5 mg of as-synthesized Au⊂UiO-66 under sonication. After mixing, a ZrCl₄ solution in DMF (0.5 mL, 30 mM) was added and stirred for 10 min. Then, 52 µL HCOOH was added in to the solution. The mixture was heated in an oven at 120 ºC for 2 h. After cooling down to room temperature, the product was collected by centrifugation and washed by fresh DMF and anhydrous methanol three times, respectively.

Synthesis of Au⊂hollow MOF-801

The as-synthesized Au⊂UiO-66@MOF-801 was re-dispersed in 1.25 mL DMF containing 0.038 mmol FA (4.4 mg) and 260 µL HCOOH under sonication. After mixing, the mixture was heated in an oven at 120 ºC for 4 h. After cooling down to room temperature, the product was
collected by centrifugation and washed by fresh DMF and anhydrous methanol three times, respectively.
Catalytic study

Catalytic hydrogenation of nitro compounds

In a typical procedure, each catalyst containing the same amount of Pt NPs (36 μg) was dispersed in 1 mL ethanol. Then a nitro compound with internal standard substance (0.025 mmol of nitrobenzene (NB) or 1-nitronaphthalene (NN)) was added. Subsequently, the mixture was transferred into a stainless-steel autoclave. The autoclave was purged with H$_2$ for 8 times, and the final H$_2$ pressure of the autoclave was set at 10 bars. The mixture was continuously stirred (600 rpm) at 50 °C for 90 min. After reaction, the autoclave was cooled down, the pressure was vented. Then, the solution was separated by filtration and analyzed by gas chromatography (GC) with n-decane as the internal standard for the hydrogenation of NB, and n-dodecane as the internal standard for the hydrogenation of NN. For the time-dependent catalysis, when reaction went on 10, 30, 60, 90,120 min, taking 50 µL reaction mixture into 1 mL ethanol each time, and then the solution was separated by filtration and analyzed by GC.

In the process of thiols poisoning catalysis, each catalyst containing the same amount of Pt NPs (36 μg) was dispersed in 1.125 mL toluene containing 0.5 μmol of ethanethiol or 1-adamantanethiol. After 10 minutes of sonication, the sample was collected by centrifugation and washed by toluene and anhydrous ethanol three times, respectively. Sequentially, the catalysts were applied for the hydrogenation of NB following the above typical catalytic procedure.

For the catalytic recycling experiment, the Pt⊂MOF-801(h) containing 36 μg Pt NPs was applied for the hydrogenation of NB following the above typical catalytic procedure. The reaction duration of the catalytic hydrogenation of nitrobenzene (NB) was changed to 30 min. Then the
catalyst was re-collected by centrifugation and washed by anhydrous ethanol three times for the next catalytic experiment. Nine cycles of catalytic experiments were carried out in this way.

When studied the catalytic stability of Pt⊂MOF-801(h), Pt⊂MOF-801(h) containing 36 μg Pt NPs was dispersed in 1 mL 1 M HCl aqueous solution at 25 °C for 1 h, 1 mL concentrated hydrochloric acid at 25 °C for 1 h, and boiling water at 120 °C for 3 h, respectively. Then, the catalysts were applied for the hydrogenation of NB and NN following the above typical catalytic procedure.

**Catalytic reaction of alkynes with HCl**

In a typical procedure, each catalyst containing the same amount of Au NPs (116 μg) was dispersed in 0.5 mL anhydrous 1,4-dioxane. Followed by an alkyne compound (0.5 mmol of 4-ethynyltoluene or 1-ethynylnaphthalene) was added. Then added 3A MS and 150 μL 4M HCl (0.6 mmol) into the solution. Subsequently, the mixture was sealed into a glass bottle and was continuously stirred (600 rpm) at 90 °C overnight (24 h). After reaction, the glass bottle was cooled down, and the solution was separated by filtration. Then, aliquots of 100 μL were taken and diluted in hexane (1 ml) for gas chromatography-mass spectrometry (GC-MS) analysis, using pure 4-ethynyltoluene or 1-ethynylnaphthalene as the external standard.
Section S3. Characterization

Transmission electron microscope (TEM) images were acquired on a JEM 1400 field-emission transmission electron microscope with voltage set at 120 kV and JEM-2100 Plus field-emission transmission electron microscope with voltage set at 200 kV. Select area electron diffraction (SAED) patterns were collected on a JEOL JEM F200 Electron Microscope operated at 200 kV. Scanning electron microscope (SEM) images were acquired on a JEOL JSM 7800F Prime SEM. Powder X-ray diffraction patterns (PXRD) were acquired on a Bruker D8 Advance diffractometer with Cu Kα radiation. Gas adsorption analysis was performed on a MicrotracBEL-Belsorp-MAXII volumetric gas adsorption analyzer. Gas chromatography (GC) was performed on an Agilent Technologies 7890B GC system equipped with a polar column of CYCLOSIL-B and flame ionization detector (FID), with inlet temperature of 250 ºC. The products have been separated by starting from 40 ºC and hold for 2 min with subsequent heating to 150 ºC at a rate of 30 ºC/min, then to 250 ºC at a rate of 20 ºC/min. Gas chromatography-mass spectrometry (GC-MS) was performed on a Thermo Fisher Scientific Trace 1300 ISQ system equipped with a polar column of TG-5MS, with inlet temperature of 280 ºC. The products have been separated by starting from 40 ºC and hold for 1 min with subsequent heating to 280 ºC at a rate of 30 ºC/min, then hold for 1 min. Inductively coupled plasma-optical emission spectroscopy (ICP-OES) experiments were carried out on a Thermo-Fisher ICP-OES Icap 7400. 1H NMR spectra was obtained on a Bruker AVANCE III HD (500 MHz) at room temperature (RT). TGA experiments were performed on a PerkinElmer TGA 8000. Samples were firstly heated to 150 ºC and retained at that temperature for 30 minutes under N₂ atmosphere to remove residual solvent and then heated to 700 ºC at a rate of 20 ºC/min under oxygen (O₂) atmosphere, and then kept 700 ºC for 10 min, and finally raised the temperature to 750 ºC with rate of 20
°C/min at O₂. FT-IR spectra were performed on a PerkinElmer FTIR Spectrometer in transmission mode in the range of 4000-500 cm⁻¹. Elemental analysis was performed on a PerkinElmer 2400 Series II CHNS/O Elemental Analyzer, the mass of the elemental analysis samples was accurately weighed by the Mettler Toledo XS105 Excellence XS Analytical Balance.

The first-order integrated rate law

The first-order integrated rate law can be written as:

\[ \ln(1-c) = -kt \]  

where \( c \) is the conversion of reactant, \( k \) (min⁻¹) is the reaction rate constant, \( t \) is the reaction time. \( k \) can be calculated by linearly fitting the \( \ln(1-c) \) vs. time data.
Section S4. Supplemental Figures and Tables

Figure S1. SEM (A) and TEM (B) images of UiO-66.
Figure S2. TEM images (A) and PXRD patterns (B) of UiO-66@MOF-801 with different UiO-66/MOF-801 growth solution ratio while keeping the precursor concentration at 15 mM and adding 184 eq. (with respect to fumaric acid) HCOOH.
Figure S3. PXRD patterns UiO-66@MOF-801 with various amount of HCOOH.

Figure S4. PXRD patterns of UiO-66@MOF-801 synthesized with increasing reaction time. The red zone highlights the characteristic diffraction peak of the \{200\} facet of MOF-801.
Figure S5. SEM (A) and TEM (B) image of 66@801.

Figure S6. Digital photographs of 66@801 before and after being treated with HCOOH in DMF.
Figure S7. FT-IR spectra of MOF-801, UiO-66, 66@801 and MOF-801(h). The band at 1506 cm$^{-1}$ is assigned to the C=C stretching vibration of the phenyl ring. This peak was only found in UiO-66 and 66@801 but not MOF-801(h) which proves the complete removal of UiO-66 core during the etching process.
Figure S8. TGA profiles for UiO-66, MOF-801, 66@801, and MOF-801(h). In the table is theoretical and actual ZrO$_2$ : MOF ratios measured from the TGA profiles.
Figure S9. $^1$H NMR spectrum of MOF-801(h) and 66@801 (500 MHz, $d^6$-DMSO), 8.04 (a, 4H), 6.63 (b, 2H). The $^1$H NMR spectrum of the digested 66@801 suggested that the molar ratio of H$_2$BDC and fumaric acid is 1 : 1.26, which is comparable to that calculated by elemental analysis (1 : 1.43) (Table S1).
Figure S10. TEM images of Pt NPs.

Figure S11. TEM and SEM images of Pt⊂UiO-66 (A) and Pt⊂MOF-801 (B). The arrow represents the diffusion distance of the reactant in the MOF particle.
Figure S12. TEM and SEM images of Pt⊂66@801 (A) and Pt⊂MOF-801(h) (B).
Figure S13. PXRD patterns of Pt⊂UiO-66, Pt⊂MOF-801, Pt⊂66@801 and Pt⊂MOF-801(h).
Figure S14. GC-FID peak analysis of catalytic conversion of nitrobenzene. Reaction condition: 0.025 mmol of nitrobenzene + 1 mL ethanol + 1.25 mg Pt⊂UiO-66, 50 °C, 10 bar H₂, 90 min.
Figure S15. GC-FID peak analysis of catalytic conversion of 1-nitronaphthalene. Reaction condition: 0.025 mmol of 1-nitronaphthalene + 1 mL ethanol + 1.25 mg Pt⊂UiO-66, 50 °C, 10 bar H₂, 90 min.
Figure S16. The hydrogenation conversion of nitrobenzene and 1-nitronaphthalene over time for Pt NPs.

Figure S17. The hydrogenation conversion of nitrobenzene over time for various catalysts.
Figure 18. The hydrogenation conversion of NB over time for Pt NPs and Pt NPs treated with formic acid (4.6 M formic acid for 4 h).

Figure S19. TEM (A) and SEM (B) image of Pt⊂MOF-801(h) after recycling 9 times.
Figure S20. TEM and SEM images of Pt⊂MOF-801 (h) after treatment with 1M HCl (A), concentrated HCl (B) and boiling water (C).
Figure S21. TEM and SEM images of Au⊂UiO-66 (A) and Au⊂MOF-801 (B).
Figure S22. TEM (A) and SEM (B) images of Au<sub>66</sub>@801.
**Figure S23.** TEM (A) and SEM (B) images of Au⊂MOF-801(h).

**Figure S24.** TEM image of Au NPs.
Figure S25. GC-MS peak analysis of catalytic conversion of 4-ethynyltoluene. Reaction condition: 0.5 mmol of 1-nitronaphthalene + 0.5 mL 1,4-dioxane + 0.6 mmol HCl + 3 Å molecular sieves + 2.5 mg Au⊂UiO-66, 90 °C, 24 h.
Figure S26. TEM (A) and SEM (B) images of Au⊂MOF-801(h) after catalysis.

Figure S27. N$_2$ adsorption-desorption isotherms at 77 K for Au⊂MOF-801(h) before and after the nucleophilic addition catalysis of HCl to terminal alkynes.
Table S1. Elemental analysis and calculated chemical formula of all MOFs.

| Sample name | Calculated chemical formula | Calculated loading (wt%) | Predicted loading (wt%) |
|-------------|-----------------------------|--------------------------|-------------------------|
|             |                             | C | H | N | C | H | N |
| UiO-66      | Zr₆O₄(OH)₄(BDC)₅.₈(DMF)₀.₉(H₂O)₀.₃₉ | 34.0 | 1.7 | 0.1 | 34.0 | 1.7 | 0.0 |
|             |                             | 8 | 1 | 0 | 8 | 5 | 8 |
| MOF-801     | Zr₆O₄(OH)₄(fumarate)₇(DMF)₀.₃(H₂O)₀.₁ | 23.1 | 0.9 | 0.3 | 23.1 | 1.3 | 0.2 |
|             |                             | 9 | 8 | 1 | 2 | 6 | 8 |
| 66@801      | Zr₆O₄(BDC)₄(fumarate)₂.₈(DMF)₀.₃ | 31.5 | 1.5 | 0.3 | 31.5 | 1.6 | 0.2 |
|             |                             | 6 | 8 | 0 | 8 | 6 | 5 |
| MOF-801(h)  | Zr₆O₄(OH)₄(BDC)₁.₁(fumarate)₅.₂(DMF)₀.₄₉ | 25.1 | 0.9 | 0.5 | 25.0 | 1.5 | 0.4 |
|             |                             | 1 | 5 | 0 | 7 | 0 | 6 |

Table S2. The BET surface area of MOFs.

| Sample name | BET surface area (m²/g) |
|-------------|-------------------------|
| UiO-66      | 1230                    |
| MOF-801     | 680                     |
| 66@801      | 914                     |
| MOF-801(h)  | 677                     |
Table S3. Pt NPs loading amount in different samples determined by ICP-OES, and the amount of each catalysts used in size selective catalysis.

| Sample name       | Loading of Pt NPs (wt %) | Amount of catalysts (mg) | Amount of Pt (μg) |
|-------------------|--------------------------|--------------------------|-------------------|
| Pt⊂UiO-66         | 2.86                     | 1.25                     | 36                |
| Pt⊂MOF-801        | 3.00                     | 1.2                      | 36                |

Note that all the Pt NPs presented in all catalysts are ~3 nm in diameter, and furthermore, each catalyst used contains the same amount of Pt NPs (36 μg). For Pt⊂66@801 and Pt⊂MOF-801(h), both are synthesized from 1.25 mg Pt⊂UiO-66 containing 36 μg Pt NPs. Such similar size and content of Pt NPs in different samples make the catalytic performance evaluation more comparable.
Table S4. Pt amount in the supernatant after filtration for the Pt NPs encapsulation reaction determined by ICP-OES, and the encapsulating efficiency of Pt NPs.

| Sample name | Pt amount in solution (mg) | Encapsulating Efficiency (%) |
|-------------|---------------------------|------------------------------|
| Pt⊂UiO-66   | 0.48                      | 92                           |
| Pt⊂MOF-801  | 0.66                      | 89                           |
**Table S5.** The conversion (%) of nitrobenzene and 1-nitronaphthalene over bare MOFs after 90 min of the hydrogenation reaction.

|                  | UiO-66 | MOF-801 | 66@801 | MOF-801(h) |
|------------------|--------|---------|--------|------------|
| Nitrobenzene     | 0.92   | 0       | 0      | 0          |
| 1-Nitronaphthalene| 1.6    | 0.50    | 0.35   | 0.44       |

**Table S6.** The mass ratio of Zr and Pt for Pt⊂UiO-66 and Pt⊂MOF-801 before and after the hydrogenation of nitrobenzene, and the mass ratio of Zr and Pt for Pt⊂MOF-801(h) before and after recycling 9 times. All the Pt and Zr amount determined by ICP-OES.

| Sample name       | The mass ratio of Zr and Pt (Zr : Pt) | Pt loading in solution (wt %) |
|-------------------|--------------------------------------|-------------------------------|
|                   | Before catalysis | After catalysis | Before catalysis | After catalysis recycling 9 times | Before catalysis | After catalysis recycling 9 times | Before catalysis | After catalysis recycling 9 times |
| Pt⊂UiO-66         | 11.44 | 11.42 | Not detectable |
| Pt⊂MOF-801        | 13.37 | 13.10 | Not detectable |
| Pt⊂MOF-801(h)     | 27.94 | 27.90 | N/A           |
**Table S7.** Au NPs loading amount in different samples determined by ICP-OES, and the amount of each catalysts used in size selective catalysis.

| Sample name     | Loading of Au NPs (wt %) | Amount of catalysts (mg) | Amount of Au (μg) |
|-----------------|--------------------------|--------------------------|-------------------|
| Au⊂UiO-66       | 4.62                     | 2.5                      | 116               |
| Au⊂MOF-801      | 1.67                     | 6.9                      | 116               |

Note that each catalyst used contains the same amount of Au NPs (116 μg). Au⊂MOF-801(h) was synthesized from 2.5 mg Au⊂UiO-66 containing 116 μg Au NPs. Such similar content of Au NPs in different samples make the catalytic performance evaluation more comparable.

**Section S5. Reference**

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