

**Supporting Information for**

**Uncovering Two Kinetic Factors in the Controlled Growth of  
Topologically Distinct Core-Shell Metal-Organic Frameworks**

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# Materials and Characterization Methods

## Materials

All reagents and solvents were obtained through commercial sources without further purification.

## Characterization

High-resolution scanning electron microscope (HRSEM) images were obtained using a JEOL JSM-7800F Prime SEM. Samples were coated with Au for 10 seconds using an SBC-12 sputter coater. Transmission electron microscope (TEM) images were acquired on a JEOL JEM 1400 plus (120 kV). Samples were first diluted 10 times using methanol. Then, a 2.0  $\mu$ l solution droplet was added onto a carbon-coated copper grid. Energy dispersive X-ray spectra (EDS) elemental mapping results were obtained on a JEM 1400 plus (120 kV). Powder X-ray diffraction (PXRD) patterns were collected on an X-ray diffractometer (Bruker D2 PHASER or D8 ADVANCE). N<sub>2</sub> sorption data at 77K was collected on a BELSORP Max II. Before gas adsorption-desorption measurement, all samples were soaked in volatile solvates to exchange the nonvolatile solvates and were activated for 10 h at 150 °C. Inductively coupled plasma optical emission spectroscopy (ICP-OES) experiments were carried out on a Thermo-Fisher ICP-OES Icap7400, with the wavelength set at Zn 466 nm. Water contact angle measurements were performed on a contact angle meter (Kino SL200K series). Before water contact angle measurements, the sample dispersed in solvent (with a relatively high concentration) was dropped onto a glass slide to form a completely covered and flat surface after the solvent was evaporated. Gas chromatography (GC) was performed on an Agilent Technologies 7890B GC system.

## Experimental Details

**Synthesis of MIL-101(Cr).** MIL-101(Cr) was synthesized according to a previously reported method with slight modification. A precursor solution was prepared by mixing terephthalic acid (H<sub>2</sub>BDC, 0.415 g, 2.5 mmol) and Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (1.0 g, 2.5 mmol) in 10 ml of deionized water. The resulting mixture was placed in a Teflon-lined autoclave and kept in an oven (200 °C) for 16 h. After cooling down to room temperature, the precipitate was collected by centrifugation and then washed several times with fresh DMF (3X) and methanol (3X). The final produce was soaked in methanol for later use.<sup>[1]</sup>

**Synthesis of MOF-801(Zr).** MOF-801(Zr) was synthesized according to a previously reported method with slight modification. A precursor solution was prepared by mixing fumaric acid (18 mmol) and ZrCl<sub>4</sub> (18 mmol) in 600 ml DMF solution containing 41.4 ml acetic acid. Then 1.8 ml triethylamine was added into the solution. The vial was capped and placed in an oven (85 °C) for 18 h. After cooling down to room temperature, the precipitate was collected by centrifugation and then washed several times with fresh DMF (3X) and methanol (3X). The final produce was soaked in methanol for later use.<sup>[2]</sup>

**Synthesis of MIL-96(Al).** MIL-96(Al) was synthesized according to a previously reported method with slight modification. Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (375 mg, 1 mmol) was dissolved in 6 ml deionized water and benzene-1,3,5-tricarboxylic acid (H<sub>3</sub>BTC, 210 mg, 1 mmol) was dissolved in 6 ml DMF, respectively. Then two solutions were mixed in a Teflon-lined autoclave. After mixing, 0.5 ml of acetic acid was added. The resulting mixture was placed in an oven (150 °C) for 2 h. After cooling down to room temperature, the precipitate was collected by centrifugation and then washed several times with fresh DMF (3X) and methanol (3X). The final produce was soaked in methanol for later use.<sup>[3]</sup>

**Synthesis of MIL-53(Cr).** MIL-53(Cr) was synthesized according to a previously reported method with slight modification. Hydrofluoric acid (48%, 34.8 μl, 2 mmol) was added to the precursor solution of terephthalic acid (H<sub>2</sub>BDC, 332 mg, 2 mmol) and Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (800 mg, 2 mmol) dissolved in 10 ml of deionized water. The resulting mixture was placed in a Teflon-lined autoclave and kept in an oven (220 °C) for 3 days. After cooling down to room temperature, the precipitate was collected by centrifugation and then washed several times with fresh DMF (3X) and methanol (3X). The final produce was soaked in methanol for later use.<sup>[4]</sup>

**Synthesis of UiO-66.** UiO-66 was synthesized according to a previously reported method with slight modification. ZrCl<sub>4</sub> (58.26 mg, 25 mM) and H<sub>2</sub>BDC (41.53 mg, 25 mM) were dissolved in 10 ml DMF followed by addition of 1.37 ml acetic acid. Then the vial was capped and placed in an oven (120 °C) for 12 h. After cooling down to room temperature, the precipitate was collected by centrifugation and then washed several times with fresh DMF (3X) and methanol (3X). The final produce was soaked in methanol for later use.<sup>[5]</sup>

**Synthesis of cubic ZIF-8.** ZIF-8 was synthesized according to a previously reported method with slight modification. An 8 ml CTAB (0.583 mM) aqueous solution, 10 ml 2-MeIM (2.68 g) aqueous solution were mixed together. After stirring for 5 min at room temperature, 10 ml Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O (274 mg) aqueous solution was added with stirring for another 5 min. Then the mixture was placed at room temperature for 3 h. The obtained ZIF-8 nanocrystals were collected by centrifugation and washed several times with methanol.<sup>[6]</sup>

**Synthesis of rhombic dodecahedron ZIF-8.** ZIF-8 was synthesized according to a previously reported method with slight modification. A 0.1 ml CTAB (0.2 M) methanol solution, 4 ml Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.06 mM) methanol solution were mixed together and then 4 ml 2-MeIM (0.25 mM) methanol solution was added. Subsequently, the mixture was allowed to react at room temperature for 24 h without stirring. Finally, the product ZIF-8 nanocrystals were collected by centrifugation and washed several times with methanol.<sup>[7]</sup>

**Synthesis of Ni-MOF-74.** Ni-MOF-74 was synthesized according to a previously reported method with slight modification. Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O (746 mg, 3 mmol) was dissolved in 30 ml deionized water and 2,5-dihydroxyterephthalic acid (549 mg, 3 mmol) was dissolved in 30 ml THF, respectively. Then two solutions were mixed in a high-pressure glass vial (200 ml) and placed in an oil bath (110 °C) for 6 h under vigorous stirring. After cooling down to room temperature, the precipitate was collected by centrifugation and then washed several times with fresh DMF (3X) and methanol (3X). The final produce was soaked in methanol for later use.<sup>[8]</sup>

**Synthesis of MIL-101(Cr)@UiO-66.** To a H<sub>2</sub>BDC solution in DMF (300 μl, 100 mM) was added 5 mg of MIL-101(Cr). After stirring for 1 min at room temperature, a ZrCl<sub>4</sub> solution in DMF (300 μl, 100 mM) was added and stirred for 10 min. The resulting mixture was placed in an oven (120 °C) for 2 h. After cooling down to room temperature, the precipitate was

collected by centrifugation and then washed several times with DMF (3X) and methanol (3X). The final produce was soaked in methanol for later use.

**Synthesis of MIL-101(Cr)@UiO-66(Hf).** To a H<sub>2</sub>BDC solution in DMF (230  $\mu$ l, 100 mM) was added 5 mg of MIL-101(Cr). After stirring for 1 min at room temperature, an HfCl<sub>4</sub> solution in DMF (230  $\mu$ l, 100 mM) was added followed by stirring for 10 min. The resulting mixture was placed in an oven (120 °C) for 2 h. After cooling down to room temperature, the precipitate was collected by centrifugation and then washed several times with fresh DMF (3X) and methanol (3X). The final produce was soaked in methanol for later use.

**Synthesis of MIL-101(Cr)@UiO-66-NH<sub>2</sub>.** To a H<sub>2</sub>BDC-NH<sub>2</sub> solution in DMF (283  $\mu$ l, 100 mM) was added 5 mg of MIL-101(Cr). After stirring for 1 min at room temperature, a ZrCl<sub>4</sub> solution in DMF (283  $\mu$ l, 100 mM) was added followed by stirring for 10 min. The resulting mixture was placed in an oven (120 °C) for 2 h. After cooling down to room temperature, the precipitate was collected by centrifugation and then washed several times with fresh DMF (3X) and methanol (3X). The final produce was soaked in methanol for later use.

**Synthesis of MIL-53(Cr)@UiO-66.** To a H<sub>2</sub>BDC solution in DMF (300  $\mu$ l, 100 mM) was added 5 mg of MIL-53(Cr). After stirring for 1 min at room temperature, a ZrCl<sub>4</sub> solution in DMF (300  $\mu$ l, 100 mM) was added followed by stirring for 10 min. The resulting mixture was placed in an oven (120 °C) for 2 h. After cooling down to room temperature, the precipitate was collected by centrifugation and then washed several times with fresh DMF (3X) and methanol (3X). The final produce was soaked in methanol for later use.

**Synthesis of MIL-96(Al)@UiO-66-NH<sub>2</sub>.** To a H<sub>2</sub>BDC-NH<sub>2</sub> solution in DMF (1.133 ml, 25 mM) was added 5 mg of MIL-96(Al). After stirring for 1 min at room temperature, a ZrCl<sub>4</sub> solution in DMF (1.133 ml, 25 mM) was added followed by stirring for 10 min. After mixing, 100  $\mu$ l acetic acid solution was added. The resulting mixture was placed in an oven (120 °C) for 2 h. After cooling down to room temperature, the precipitate was collected by centrifugation and then washed several times with fresh DMF (3X) and methanol (3X). The final produce was soaked in methanol for later use.

**Synthesis of MOF-801@UiO-66.** To a H<sub>2</sub>BDC solution in DMF (720  $\mu$ l, 25 mM) was added 5 mg of MOF-801. After stirring for 1 min at room temperature, a ZrCl<sub>4</sub> solution in DMF (720  $\mu$ l, 25 mM) was added followed by stirring for 10 min. After mixing, 720  $\mu$ l benzoic acid DMF solution (30 equivalents) was added. The resulting mixture was placed in an oven (120 °C) for 4 h. After cooling down to room temperature, the precipitate was collected by centrifugation and then washed several times with fresh DMF (3X) and methanol (3X). The final produce was soaked in methanol for later use.

**Synthesis of Ni-MOF-74@UiO-66-NH<sub>2</sub>.** To a H<sub>2</sub>BDC-NH<sub>2</sub> solution in DMF (283  $\mu$ l, 100 mM) was added 5 mg of Ni-MOF-74. After stirring for 1 min at room temperature, a ZrCl<sub>4</sub> solution in DMF (283  $\mu$ l, 100 mM) was added followed by stirring for 10 min. The resulting mixture was placed in an oven (120 °C) for 2 h. After cooling down to room temperature, the precipitate was collected by centrifugation and then washed several times with fresh DMF (3X) and methanol (3X). The final produce was soaked in methanol for later use.

**Synthesis of UiO-66@MOF-801.** To a fumaric acid solution in DMF (365  $\mu$ l, 200 mM) was added 5 mg of UiO-66. After stirring for 1 min at room temperature, a ZrOCl<sub>2</sub>.8H<sub>2</sub>O solution in DMF (365  $\mu$ l, 200 mM) was added followed by stirring for 10 min. After mixing, 334  $\mu$ l acetic acid solution was added. The resulting mixture was placed in an oven (120 °C) for 4 h. After cooling down to room temperature, the precipitate was collected by centrifugation and then washed several times with fresh DMF (3X) and methanol (3X). The final produce was soaked in methanol for later use.

**Synthesis of UiO-66@ZIF-8.** To a 2-methylimidazole (MIM) solution in methanol (914  $\mu$ l, 1.344 M) was added 5 mg of UiO-66. After stirring for 5 minutes, a Zn(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O solution in methanol (914  $\mu$ l, 24 mM) was added followed by stirring for 12 hours at room temperature. The solid was then collected, washed with methanol 3 times, and re-dispersed in methanol.

**Synthesis of MIL-101(Cr)@MOF-801.** To a fumaric acid solution in DMF (730  $\mu$ l, 30 mM) was added 5 mg of MIL-101(Cr). After stirring for 1 min at room temperature, a ZrCl<sub>4</sub> solution in DMF (730  $\mu$ l, 30 mM) was added followed by stirring for 10 min. The resulting mixture was placed in an oven (120 °C) for 4 h. After cooling down to room temperature, the precipitate was collected by centrifugation and then washed several times with fresh DMF (3X) and methanol (3X). The final produce was soaked in methanol for later use.

**Synthesis of MIL-101(Cr)@UiO-66(Zr)@MOF-801(Hf).** To a fumaric acid solution in DMF (365  $\mu$ l, 200 mM) was added 5 mg of MIL-101(Cr)@UiO-66(Zr). After stirring for 1 min at room temperature, a HfCl<sub>4</sub> solution in DMF (365  $\mu$ l, 200 mM)

was added followed by stirring for 10 min. After mixing, 334  $\mu\text{l}$  acetic acid solution was added. The resulting mixture was placed in an oven (120  $^{\circ}\text{C}$ ) for 4 h. After cooling down to room temperature, the precipitate was collected by centrifugation and then washed several times with fresh DMF (3X) and methanol (3X). The final produce was soaked in methanol for later use.

**Synthesis of hollow ZIF-8@UiO-66-NH<sub>2</sub>.** To a H<sub>2</sub>BDC-NH<sub>2</sub> solution in DMF (283  $\mu\text{l}$ , 100 mM) was mixed with 434  $\mu\text{l}$  ZIF-8 DMF solution. After stirring for 1 min at room temperature, a ZrCl<sub>4</sub> solution in DMF (283  $\mu\text{l}$ , 100 mM) was added followed by stirring for another 1 min. The resulting mixture was placed in an oven (120  $^{\circ}\text{C}$ ) for 2 h. After cooling down to room temperature, the precipitate was collected by centrifugation and then washed several times with fresh DMF (3X) and methanol (3X). The final produce was soaked in methanol for later use.

**Synthesis of ZIF-8@UiO-66-NH<sub>2</sub>.** To a H<sub>2</sub>BDC-NH<sub>2</sub> solution in DMF (28  $\mu\text{l}$ , 100 mM) was added 200  $\mu\text{l}$  ZIF-8 DMF solution. After stirring for 1 min at room temperature, a ZrCl<sub>4</sub> solution in DMF (28  $\mu\text{l}$ , 100 mM) was added followed by stirring for another 1 min. The resulting mixture was placed in an oven (120  $^{\circ}\text{C}$ ) for 2 h. After cooling down to room temperature, the precipitate was collected by centrifugation and then washed several times with fresh DMF (3X) and the ZIF-8@AZC (amorphous Zr-ligand complex) product was redispersed in DMF.

A H<sub>2</sub>BDC-NH<sub>2</sub> solution in DMF (28  $\mu\text{l}$ , 100 mM) was added to 200  $\mu\text{l}$  ZIF-8@Zr-Complex DMF solution. After stirring for 1 min at room temperature, a ZrCl<sub>4</sub> solution in DMF (28  $\mu\text{l}$ , 100 mM) was added followed by stirring for another 1 min. The resulting mixture was placed in an oven (120  $^{\circ}\text{C}$ ) for 2 h. After cooling down to room temperature, the precipitate was collected by centrifugation and then washed several times with fresh DMF (3X) and methanol (3X). The final produce was soaked in methanol for later use.

**Synthesis of Pt nanoparticles (NPs).** Pt NPs were synthesized according to the reported method.<sup>[9]</sup> Firstly, Solution 1 was prepared by dissolving PVP (311 mg) in a chilled ( $\sim 5^{\circ}\text{C}$ ) aqueous solution of H<sub>2</sub>PtCl<sub>6</sub> (4.0 mM, 35 ml). Solution 2 was prepared by dissolving NaBH<sub>4</sub> (26.5 mg) in a chilled ( $\sim 5^{\circ}\text{C}$ ) aqueous solution (35 ml) of PVP (311 mg). Finally, solutions 1 and 2 were mixed in a 100 ml flask placed in an ice bath. After stirring for 5 min, the Pt NPs were collected by centrifugation and subsequently washed by acetone (3X) and DMF (3X). The final produce was soaked in DMF for later use.

**Synthesis of MIL-101(Cr)@Pt.** MIL-101(Cr)@Pt was synthesized according to the literature with some modification.<sup>[10]</sup> A 5 ml Pt NP solution was added dropwise into a 5 ml DMF solution of MIL-101(Cr) under vigorous stirring. The mixture was kept stirring for 2 h. MIL-101(Cr)@Pt was collected by centrifugation and washed twice with ethanol. Finally, MIL-101(Cr)@Pt was redispersed in 20 ml ethanol, which was directly used as the catalyst for size selective catalysis. The obtained MIL-101(Cr)@Pt after centrifugation was also washed twice with DMF and redispersed in 20 ml DMF for subsequent synthesis of core-shell nanostructures.

**Synthesis of supported MIL-101(Cr)@Pt@UiO-66.** To a H<sub>2</sub>BDC solution in DMF (300  $\mu\text{l}$ , 100 mM) was added a DMF solution containing 5 mg of MIL-101(Cr)@Pt. After stirring for 1 min at room temperature, a ZrCl<sub>4</sub> solution in DMF (300  $\mu\text{l}$ , 100 mM) was added followed by stirring for 10 min. The resulting mixture was placed in an oven (120  $^{\circ}\text{C}$ ) for 2 h. After cooling down to room temperature, the precipitate was collected by centrifugation and then washed several times with fresh DMF (3X) and ethanol (3X). The final produce was soaked in ethanol for later use.

**Synthesis of supported MIL-101(Cr)@Pt@UiO-66-NH<sub>2</sub>.** To a H<sub>2</sub>BDC-NH<sub>2</sub> solution in DMF (283  $\mu\text{l}$ , 100 mM) was added a DMF solution containing 5 mg of MIL-101(Cr)@Pt. After stirring for 1 min at room temperature, a ZrCl<sub>4</sub> solution in DMF (283  $\mu\text{l}$ , 100 mM) was added followed by stirring for 10 min. The resulting mixture was placed in an oven (120  $^{\circ}\text{C}$ ) for 2 h. After cooling down to room temperature, the precipitate was collected by centrifugation and then washed several times with fresh DMF (3X) and ethanol (3X). The final produce was soaked in ethanol for later use.

**Synthesis of supported UiO-66@Pt.** UiO-66@Pt was synthesized according to the literature with some modification.<sup>[10]</sup> A 5 ml Pt NP solution was added dropwise into a 5 ml ethanol solution of UiO-66(Zr) under vigorous stirring. The mixture was kept stirring for 3 h. UiO-66@Pt was collected by centrifugation and washed twice with ethanol. The obtained UiO-66@Pt after centrifugation was also washed twice with DMF and redispersed in 20 ml DMF for subsequent synthesis of core-shell nanostructures.

**Synthesis of supported UiO-66@Pt@MOF-801.** To a fumaric acid solution in DMF (365  $\mu\text{l}$ , 200 mM) was added a DMF solution containing 5 mg of UiO-66@Pt. After stirring for 1 min at room temperature, a ZrCl<sub>4</sub> solution in DMF (365  $\mu\text{l}$ , 200 mM) was added followed by stirring for 10 min. After mixing, 334  $\mu\text{l}$  acetic acid was added. The resulting mixture was placed in an oven (120  $^{\circ}\text{C}$ ) for 4 h. After cooling down to room temperature, the precipitate was collected by

centrifugation and then washed several times with fresh DMF (3X) and ethanol (3X). The final produce was soaked in ethanol for later use.

**Post-synthetic modification of ZIF-8@UiO-66-NH<sub>2</sub>.** Firstly, 10 mg of ZIF-8@UiO-66-NH<sub>2</sub> was added to a 5 ml round-bottomed flask. Then, the system was immediately inflated with inert nitrogen after pumped to vacuum. Next, 33.8  $\mu$ l of stearoyl chloride in dried tetrahydrofuran (550  $\mu$ l) was injected through a syringe. After stirring for 1 min, 14  $\mu$ l of triethylamine was injected via a dropwise manner to the above solution, and the mixture was further stirred at ambient temperature for 12 h. Finally, the precipitates were isolated by centrifugation and fully rinsed by tetrahydrofuran with subsequent air drying.<sup>[11]</sup>

**Catalytic study.** In a typical procedure, each sample containing the same amount of Pt NPs (0.2 mg) was dispersed in 1 ml ethanol. Then a nitro compound (0.1 mmol of nitrobenzene (NB), 2,3-dimethyl nitrobenzene (DMNB), or 1-nitronaphthalene (NN)) was added. Subsequently, the mixture was transferred into a Teflon-lined stainless-steel autoclave. The autoclave was purged with H<sub>2</sub> for 8 times, and the final H<sub>2</sub> pressure of the autoclave was set at 20 bars. The mixture was continuously stirred (500 rpm) at 50 °C for 150 min. After that, the reaction mixture was filtered through a Nylon filter membrane (0.22  $\mu$ m), and then was analyzed by GC.

## Supplementary Figures

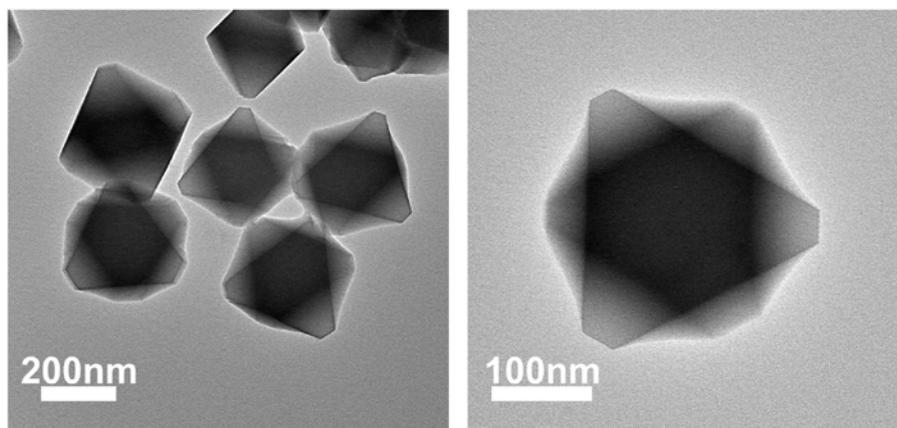


Fig. S1. TEM images of MIL-101(Cr).

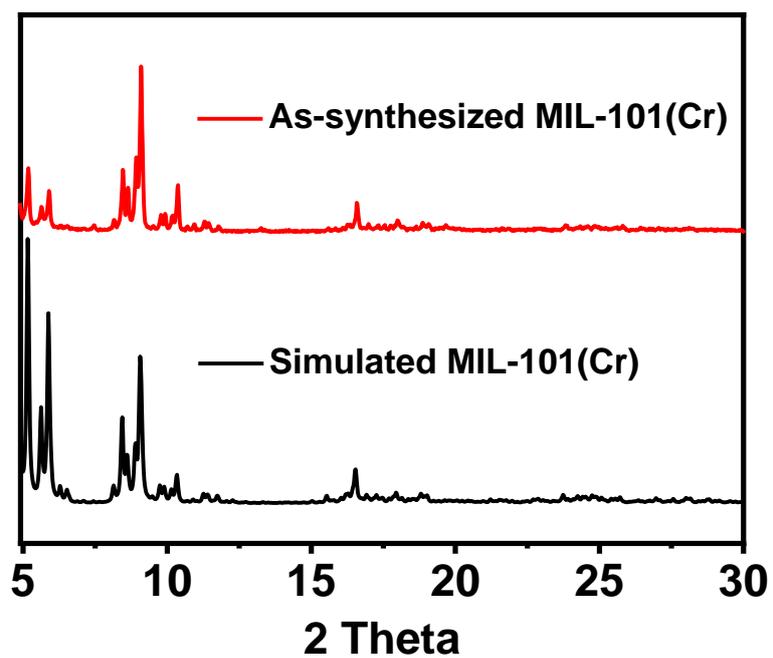


Fig. S2. PXRD patterns of MIL-101(Cr).

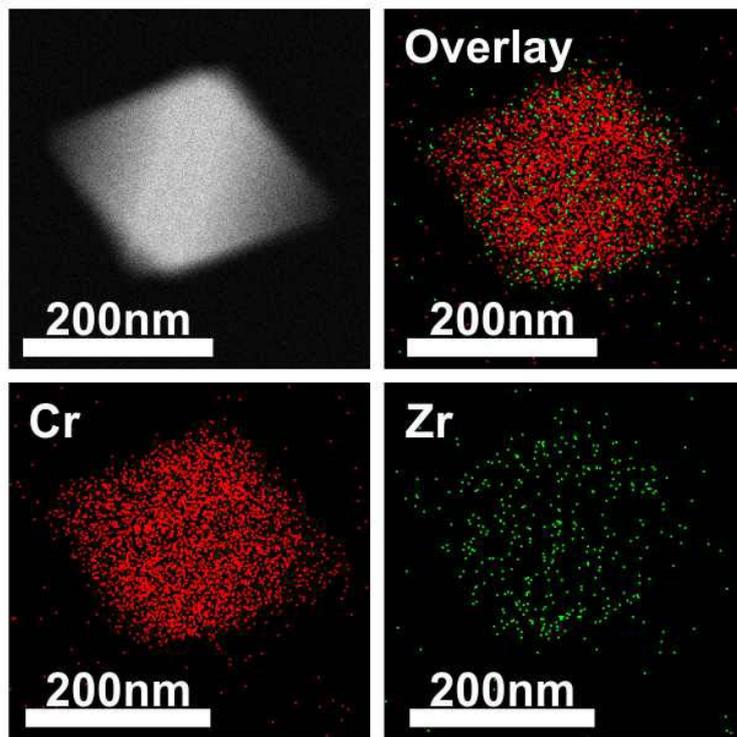


Fig. S3. EDS elemental mapping images of MIL-101(Cr)@UiO-66.

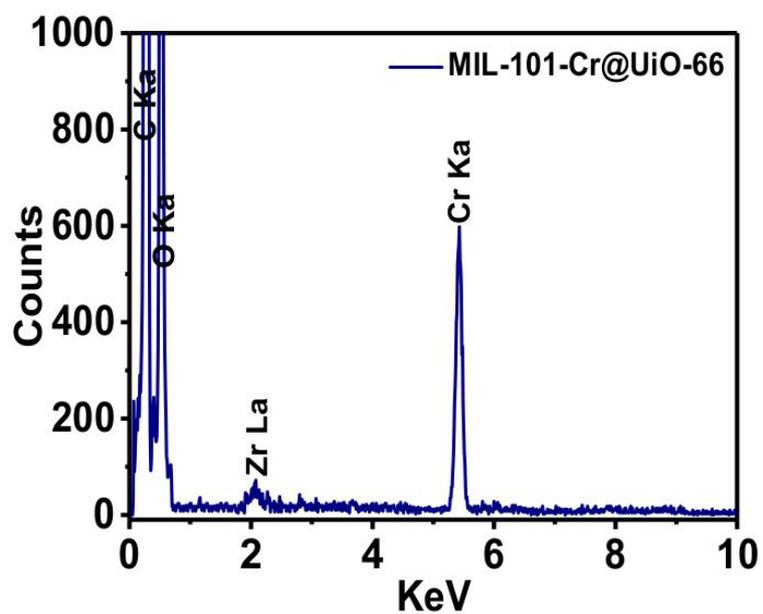
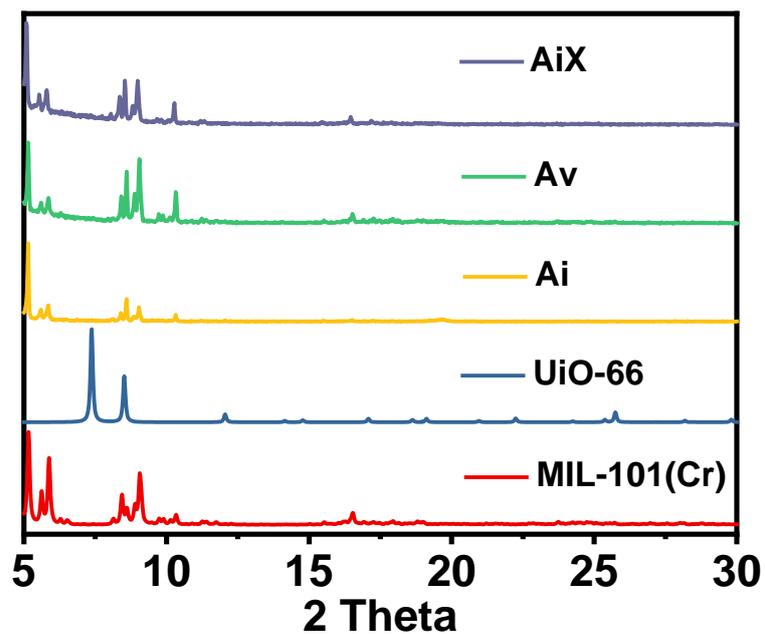
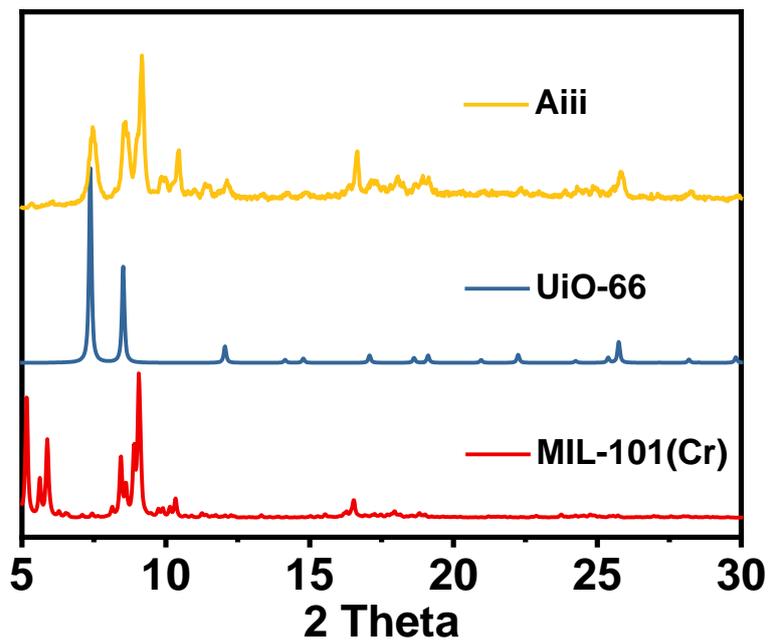


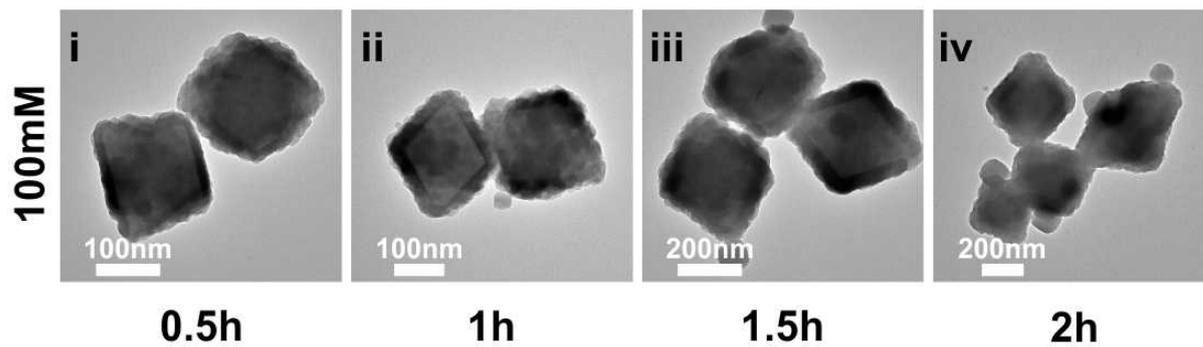
Fig. S4. EDS spectrum of MIL-101(Cr)@UiO-66.



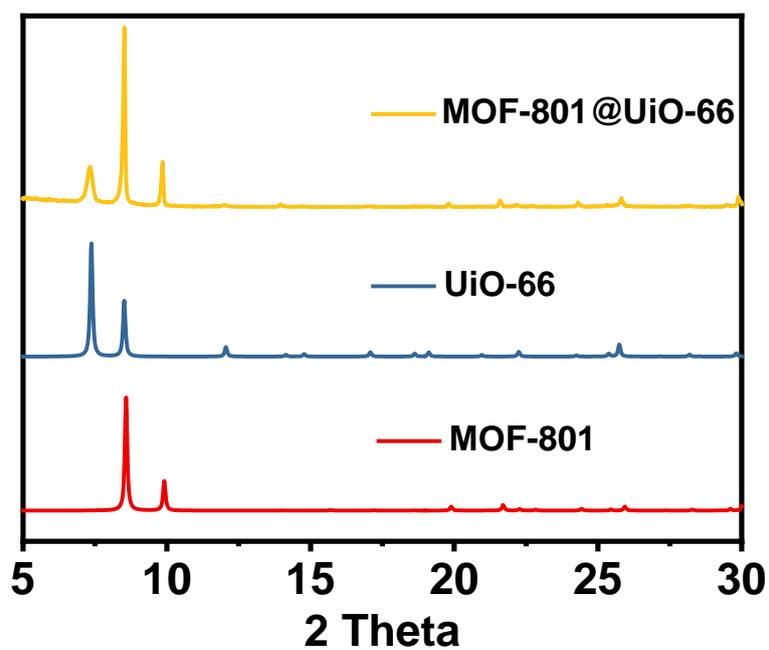
**Fig. S5.** PXRD pattern of MIL-101(Cr)@UiO-66 (Ai, Av, Aix in Figure 1) and simulated patterns of UiO-66 and MIL-101(Cr).



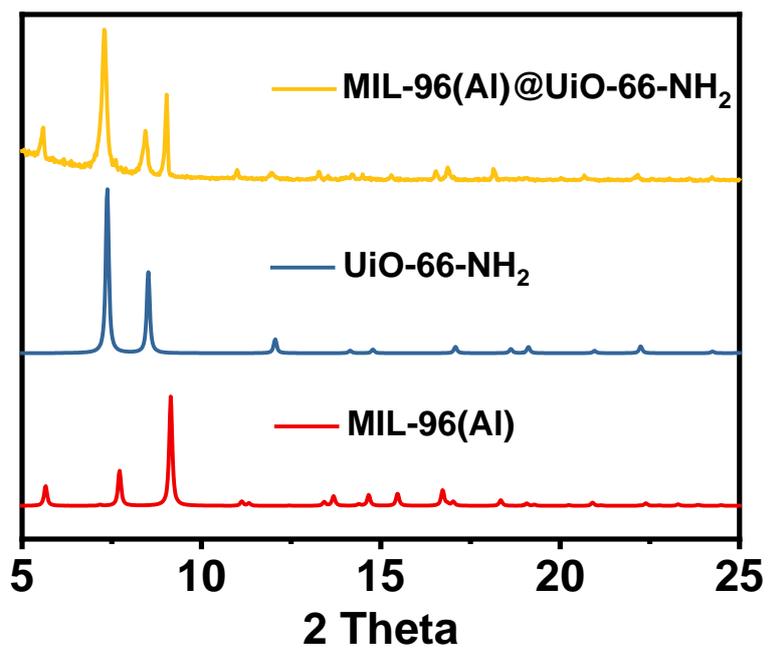
**Fig. S6.** PXRD pattern of MIL-101(Cr)@UiO-66 (Aiii in Figure 1) and simulated patterns of UiO-66 and MIL-101(Cr).



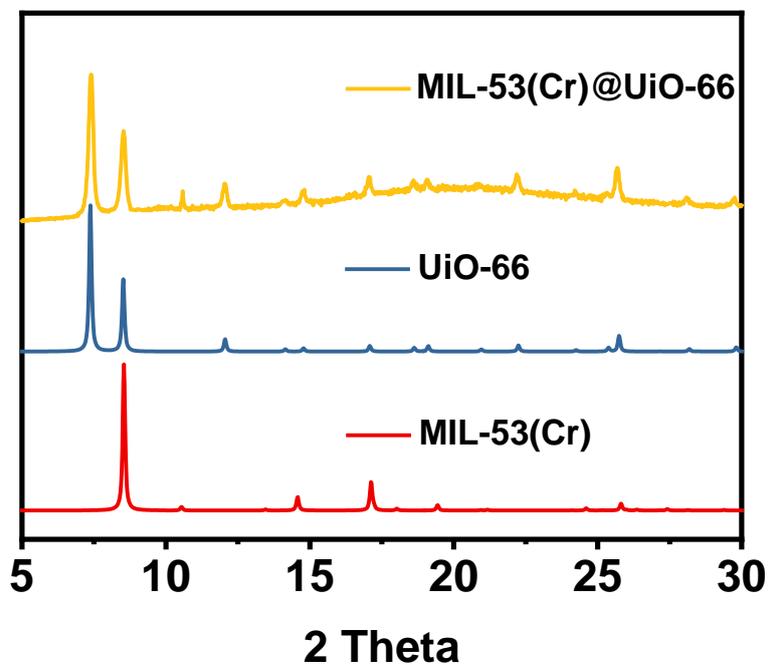
**Fig. S7.** TEM images of MIL-101(Cr)@ UiO-66. Extending the growth time of UiO-66 on MIL-101(Cr) core from 0.5 h to 1 h, 1.5 h, 2 h led to an increase of shell thickness from 13 nm to 27 nm, 46 nm, 69 nm.



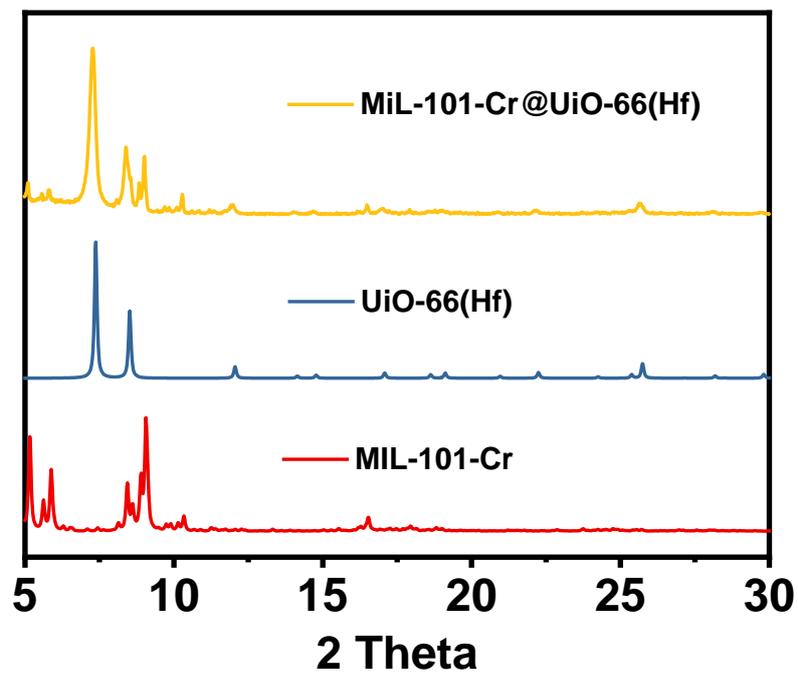
**Fig. S8.** PXRD pattern of MOF-801@UiO-66 and simulated patterns of UiO-66 and MOF-801.



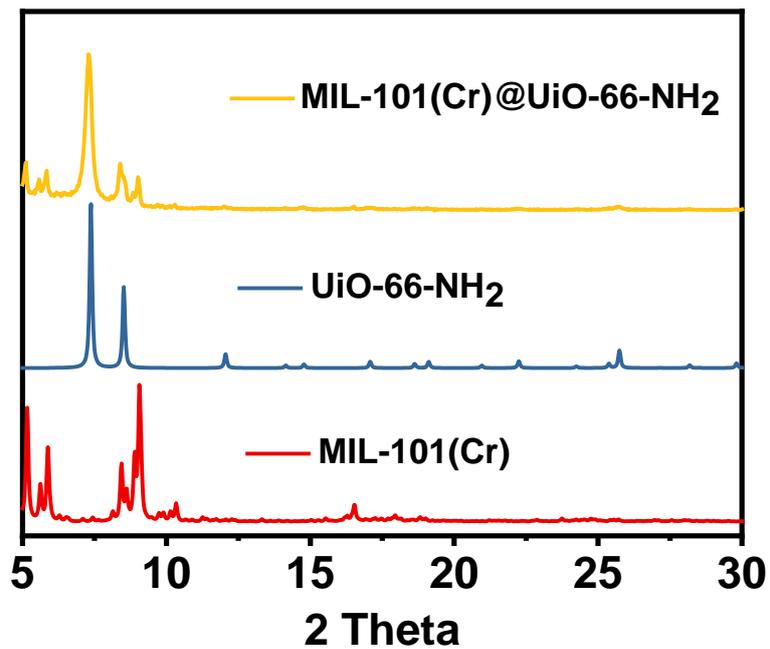
**Fig. S9.** PXRD pattern of MIL-96(Al)@UiO-66-NH<sub>2</sub> and simulated patterns of UiO-66-NH<sub>2</sub> and MIL-96(Al).



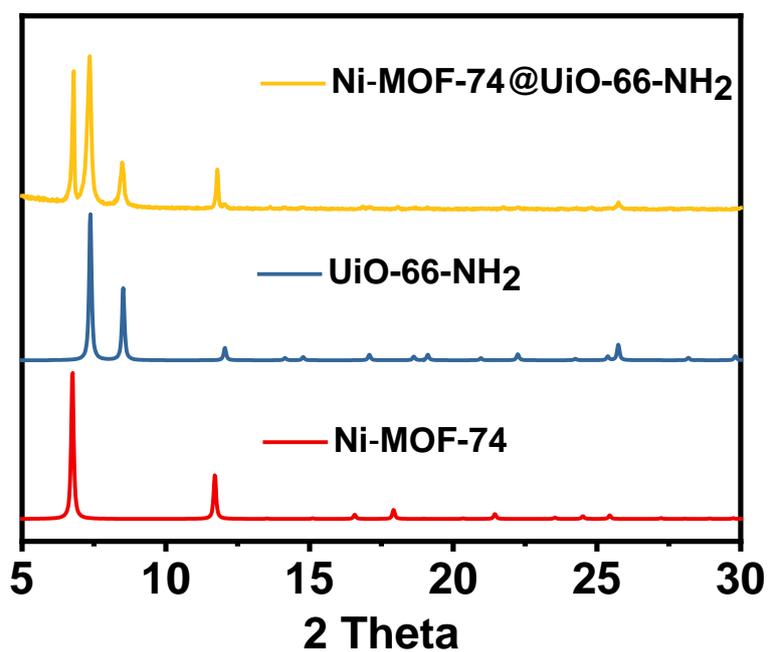
**Fig. S10.** PXRD pattern of MIL-53(Cr)@UiO-66 and simulated patterns of UiO-66 and MIL-53(Cr).



**Fig. S11.** PXRD pattern of MIL-101(Cr)@UiO-66(Hf) and simulated patterns of UiO-66(Hf) and MIL-101(Cr).



**Fig. S12.** PXRD pattern of MIL-101(Cr)@UiO-66-NH<sub>2</sub> and simulated patterns of UiO-66-NH<sub>2</sub> and MIL-101(Cr).



**Fig. S13.** PXRD pattern of Ni-MOF-74@UiO-66-NH<sub>2</sub> and simulated patterns of UiO-66-NH<sub>2</sub> and Ni-MOF-74.

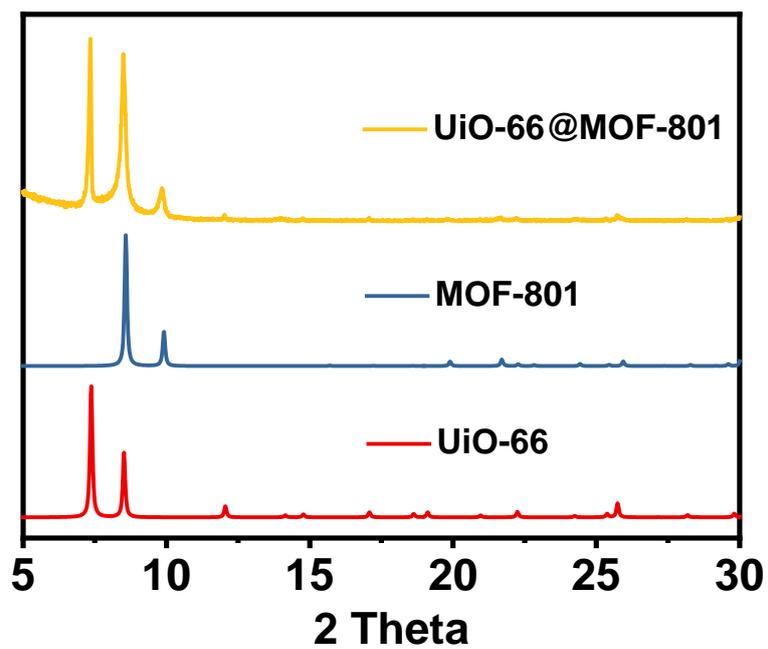


Fig. S14. PXRD pattern of UiO-66@MOF-801 and simulated patterns of MOF-801 and UiO-66.

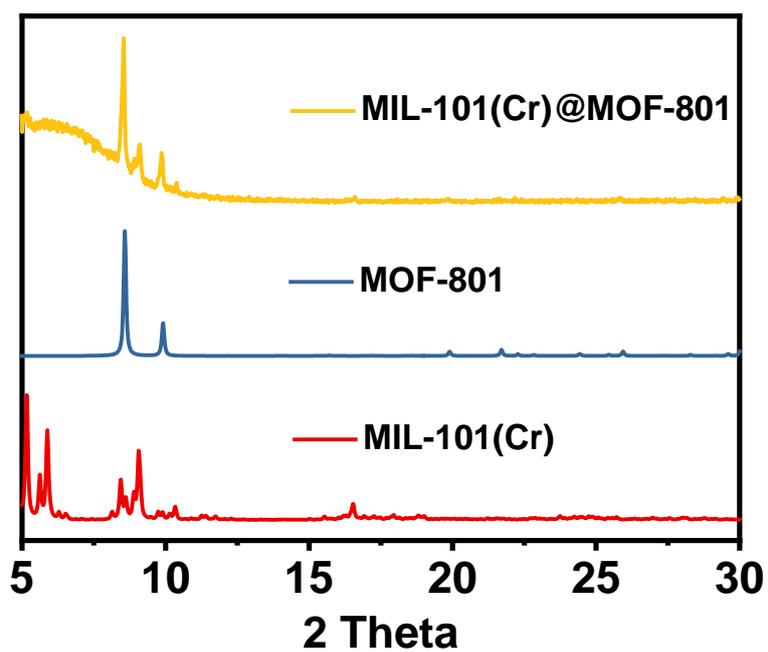
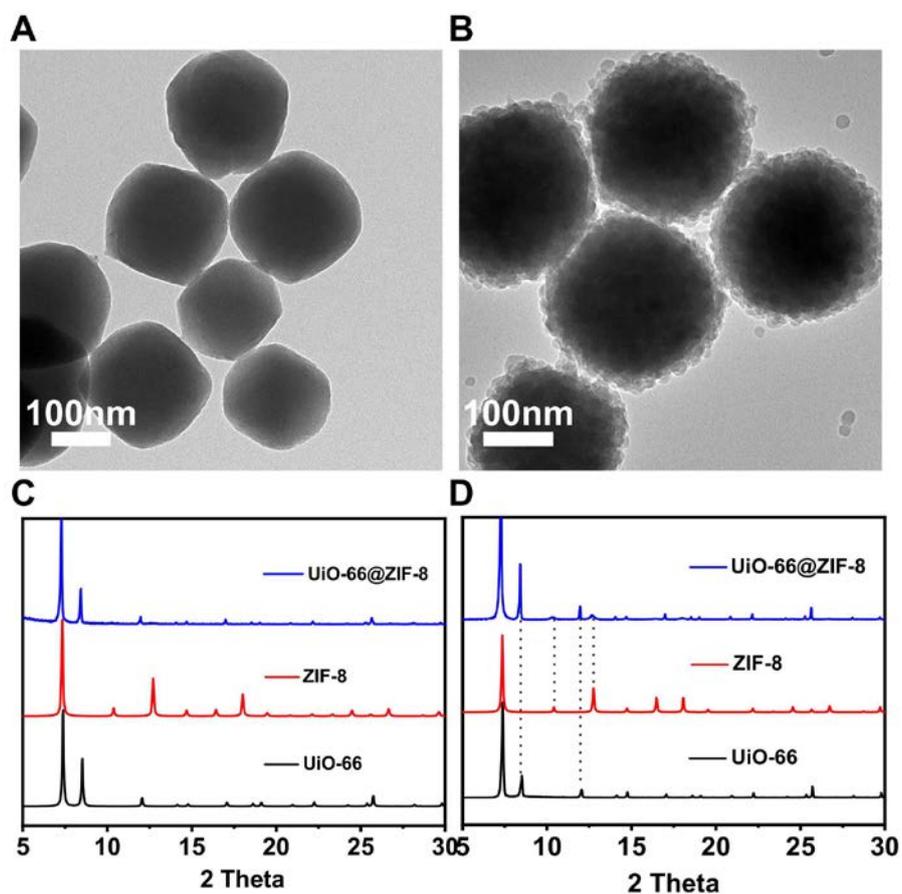


Fig. S15. PXRD pattern of MIL-101(Cr)@MOF-801 and simulated patterns of MOF-801 and MIL-101(Cr).



**Fig. S16.** The TEM image (A) and PXRD patterns (C) of UiO-66 particles after ZIF-8 shell growth (24 mM  $\text{Zn}(\text{NO}_3)_2$ ; 576 mM methylimidazole); The TEM image (B) and PXRD patterns (D) of UiO-66 particles after ZIF-8 shell growth (24 mM  $\text{Zn}(\text{NO}_3)_2$  1.344 M methylimidazole).

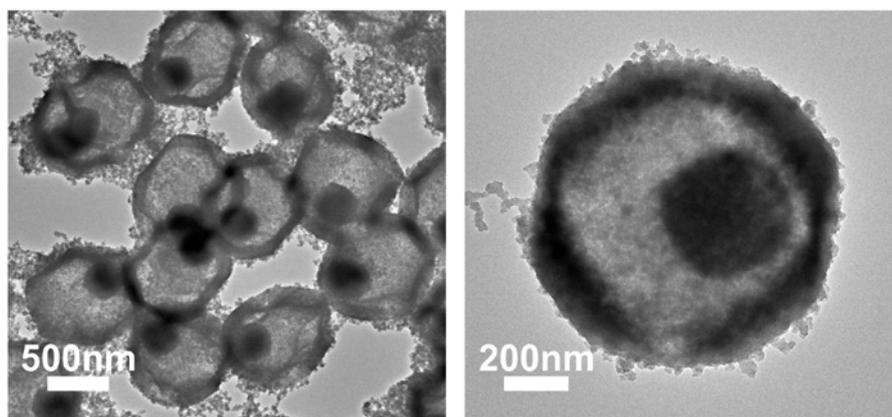


Fig. S17. TEM images of yolk-shell ZIF-8@UiO-66-NH<sub>2</sub>.

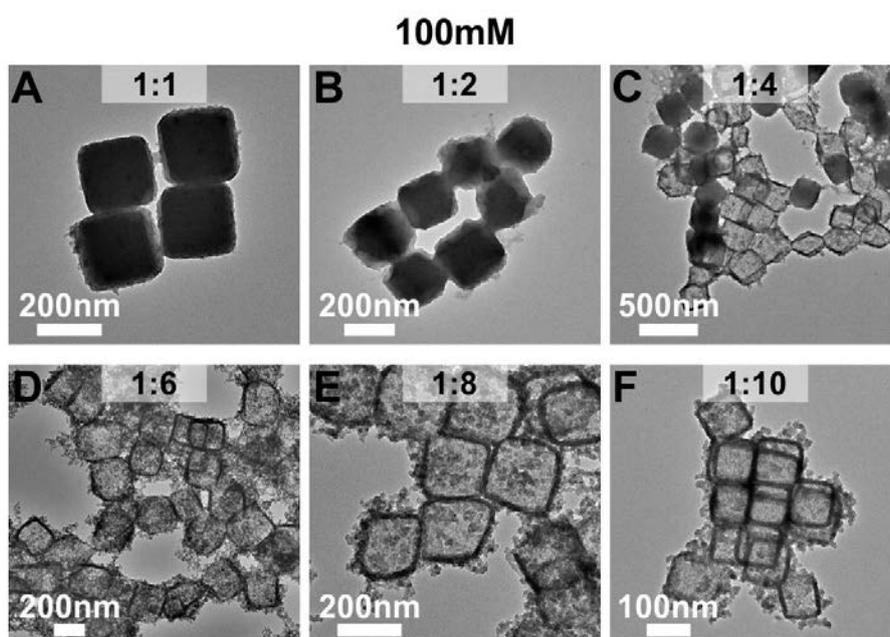
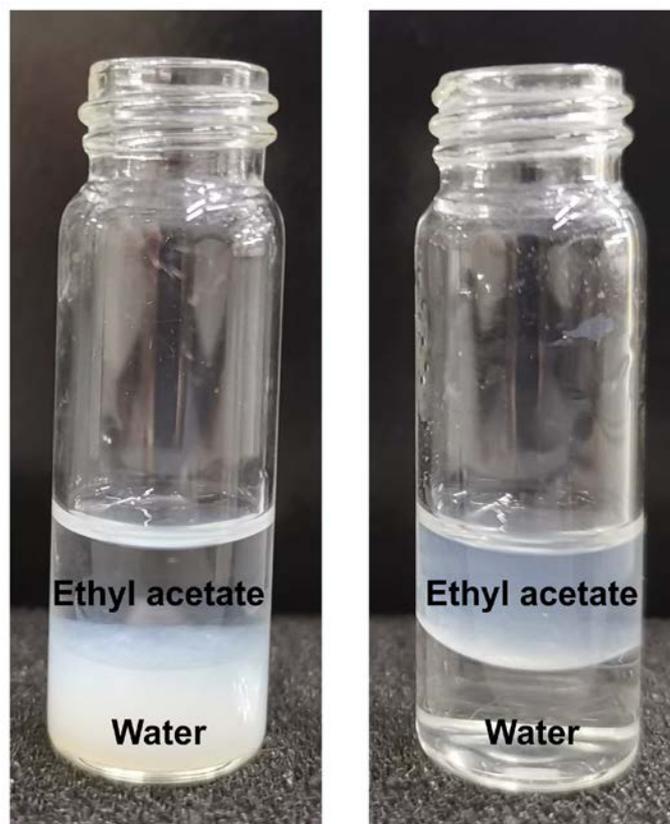
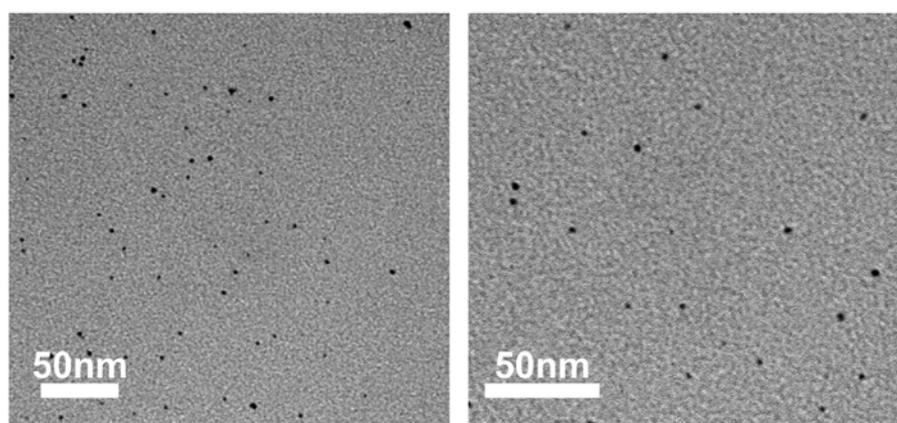


Fig. S18. TEM images of ZIF-8@UiO-66-NH<sub>2</sub> grown with various ZIF-8/UiO-66-NH<sub>2</sub> growth ratio.

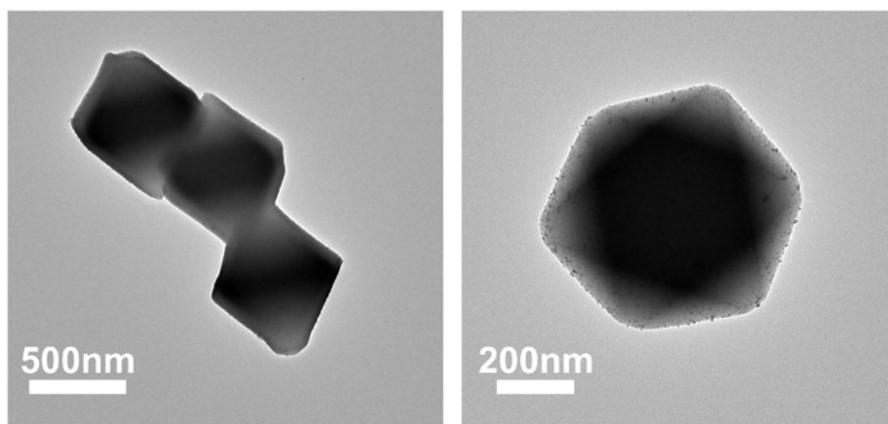


ZIF-8@UiO-66-NH<sub>2</sub>    ZIF-8@UiO-66-NH-stearoyl

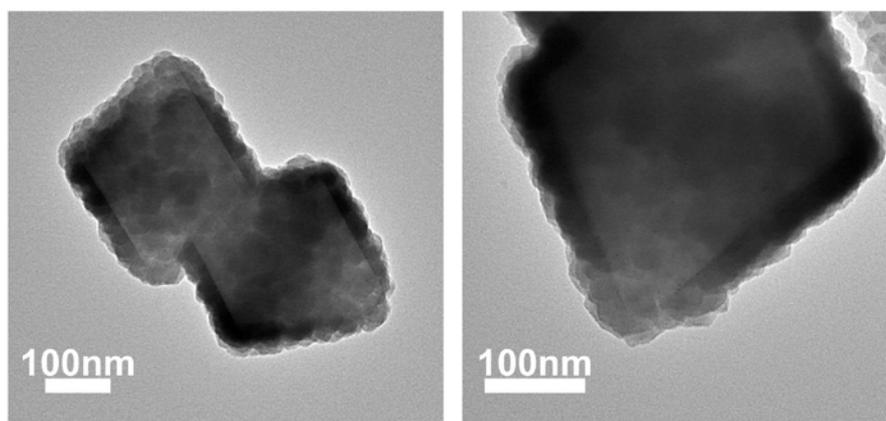
**Fig. S19.** Picture of non-functionalized ZIF-8@UiO-66-NH<sub>2</sub> (left) and alkane modified ZIF-8@UiO-66-NH<sub>2</sub> (right).



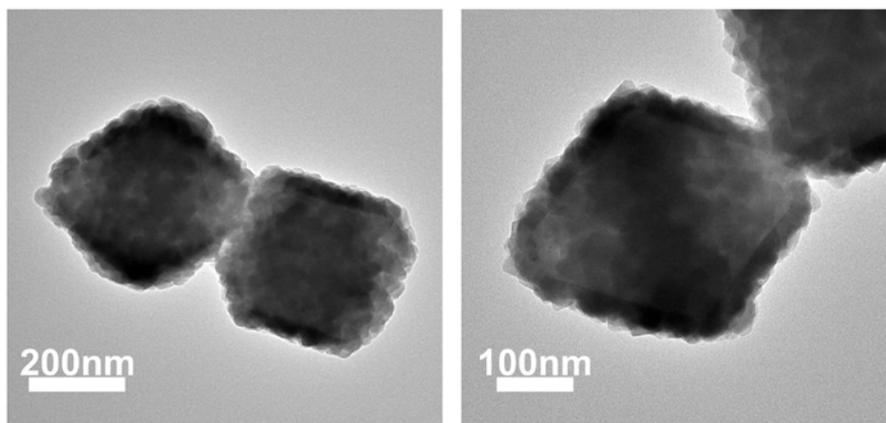
**Fig. S20.** TEM images of Pt NPs.



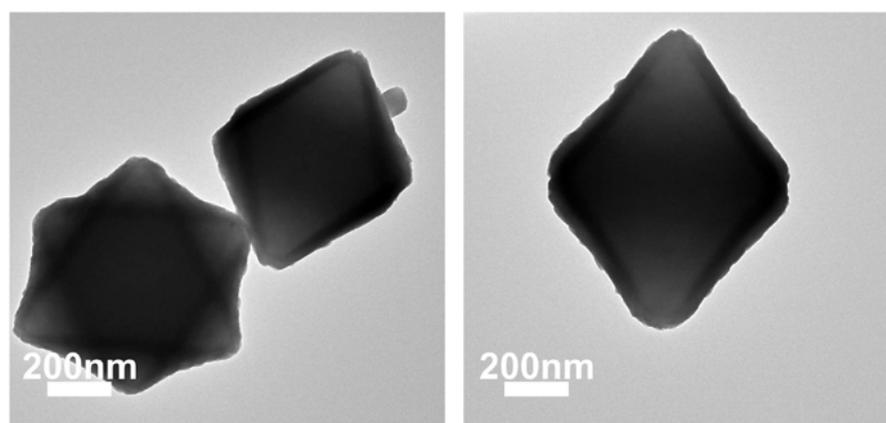
**Fig. S21.** TEM images of UiO-66@Pt.



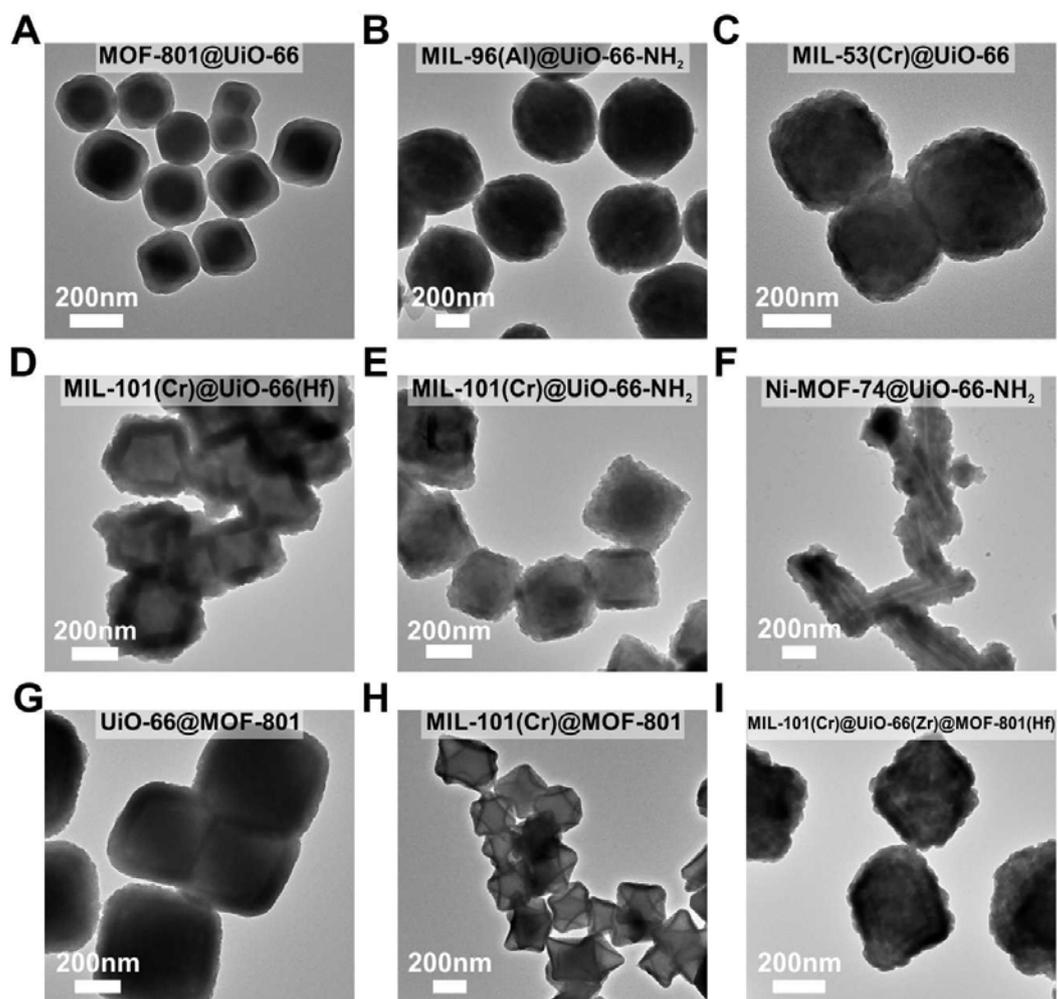
**Fig. S22.** TEM images of MIL-101(Cr)@Pt@UiO-66.



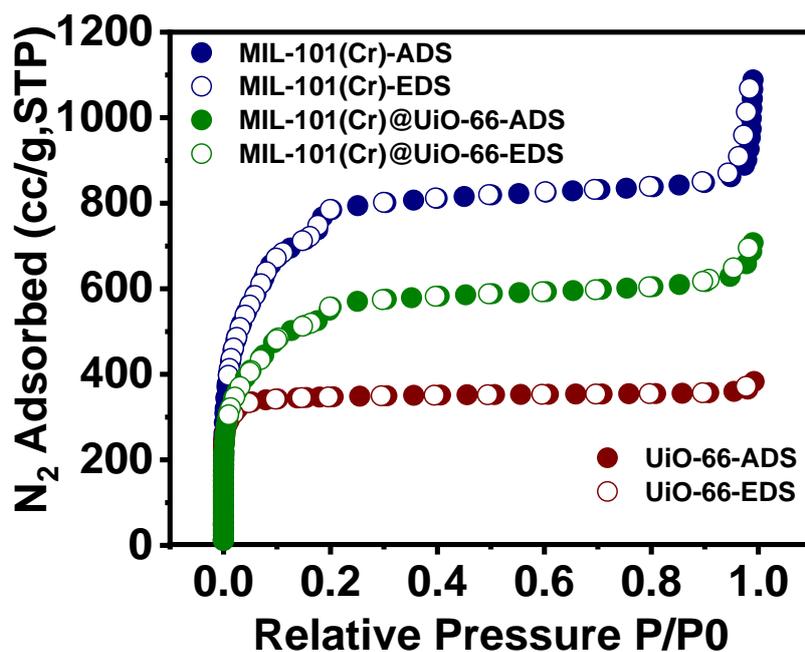
**Fig. S23.** TEM images of MIL-101(Cr)@Pt@UiO-66-NH<sub>2</sub>.



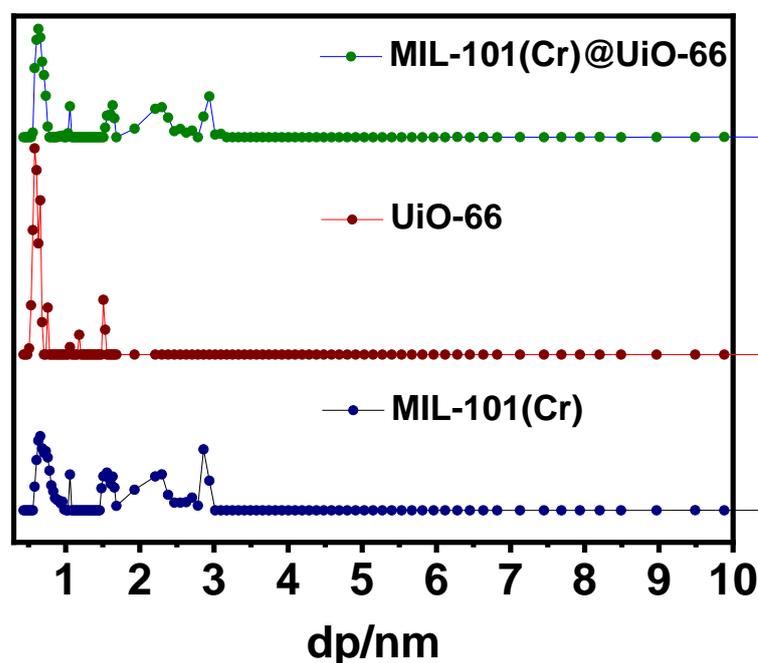
**Fig. S24.** TEM images of UiO-66@Pt@MOF-801.



**Fig. S25.** TEM images of (A) MOF-801@UiO-66, (B) MIL-96(Al)@UiO-66-NH<sub>2</sub>, (C) MIL-53(Cr)@UiO-66, (D) MIL-101(Cr)@UiO-66(Hf), (E) MIL-101(Cr)@UiO-66-NH<sub>2</sub>, (F) Ni-MOF-74@UiO-66-NH<sub>2</sub>, (G) UiO-66@MOF-801, (H) MIL-101(Cr)@MOF-801 and (I) MIL-101(Cr)@UiO-66(Zr)@MOF-801(Hf);



**Fig. S26.** N<sub>2</sub> adsorption-desorption isotherms (77 K) of MIL-101(Cr) (navy), MIL-101(Cr)@UiO-66 (green), and UiO-66 (red).



**Fig. S27.** Pore size distribution of MIL-101(Cr), MIL-101(Cr)@UiO-66 and UiO-66 is calculated by non-local density functional theory (NLDFT)/grand canonical Monte Carlo simulation (GCMC) method.

## Supplementary Tables

**Table S1:** Pt loading amount in different samples determined by ICP-OES, and the amount of each catalysts used in size selective catalysis.

Samples	Pt (wt. %)	Amount of catalysts (mg)	Amount of Pt (mg)	shell thickness (nm)
MIL-101(Cr)@Pt	4.7	4.3	0.20	/
MIL-101(Cr)@Pt@UiO-66	4.2	4.8	0.20	34
MIL-101(Cr)@Pt@UiO-66-NH <sub>2</sub>	4.0	5.0	0.20	36
UiO-66@Pt@MOF-801	2.7	7.5	0.20	38

Note that all the Pt NPs presented in all catalysts are ~2.9 nm in diameter, and furthermore, each catalyst used contains the same amount of Pt NPs (0.20 mg). Such similar size and content of Pt NPs in different samples make the catalytic performance evaluation more comparable.

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