

Supporting Information for

Hierarchically porous UiO-66: Facile synthesis, characterization and application

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1. Experimental section

1.1 Materials

Zirconium dichloride oxide octahydrate (99.9%) was purchased from Beantown Chemical. Terephthalic acid (>99%) was purchased from TCI. Zirconium (IV) chloride (98%), Methanol, Furfural (99%) and Rhodamine 6G were purchased from Alfa Aesar. N,N-Dimethylformamide (DMF) was purchased from EMD Millipore Corporation. All the chemicals were used without further purification. TCPP was synthesized according to the literature.¹

1.2 Experimental procedures

Typical procedure for the synthesis of UiO-66

Microporous UiO-66 was synthesized according to the literature with some modification.² Typically, ZrCl₄ (0.053 g, 0.227 mmol) and 1,4-benzenedicarboxylic acid (H₂BDC) (0.034 g, 0.227 mmol) were dissolved in DMF (25 mL) at room temperature. The solution was then sealed in a 30 mL vial and maintained at 120 °C for 24 h. After cooling down to room temperature, the precipitate was recovered by centrifugation and washed with DMF. Then the solid was soaked and washed using methanol for several times before dried in vacuum oven.

The synthetic procedure of hierarchically porous UiO-66 was as follows. ZrOCl₂·8H₂O was used instead of ZrCl₄. To study the influence of precursor ratios, H₂BDC (0.034 g, 0.227 mmol) was dissolved in DMF (25 mL) with the amount of ZrOCl₂·8H₂O ranging from molar ratio ZrOCl₂·8H₂O/H₂BDC=0.5 to 1.5 at room temperature. To study the influence of synthetic temperature, equivalent molar of ZrOCl₂·8H₂O and H₂BDC was used with the synthetic temperature of 100, 120, 130, 150 °C, respectively. Typically, for the synthesis of UiO-66-150, ZrOCl₂·8H₂O (0.073 g, 0.227 mmol) and H₂BDC (0.034 g, 0.227 mmol) was dissolved in DMF (25 mL) at room temperature. The solution was then sealed in a 30 mL vial and maintained at 120 °C for 48 h. After cooling down to room temperature, the precipitate was recovered by centrifugation and washed with DMF. Then the solid was soaked and washed using methanol for several times before dried in vacuum oven.

Uptake of large molecules

For uptake of rhodamine 6G, 15 mg rhodamine 6G was dissolved in 1 mL DMF. 20 mg UiO-66-150 was soaked in the solution and shaking overnight at room temperature. Then the mixture was centrifuged and washed with DMF until no rhodamine 6G was detected in the supernatant.

For uptake of porphyrin TCPP, 6 mg TCPP was dissolved in 1.5 mL DMF. 30 mg UiO-66-150 was soaked in the solution. After shaking overnight at room temperature, the mixture was centrifuged and washed with DMF under heat for several times until no characteristic peaks of TCPP were detected in the supernatant.

Microporous UiO-66 was used to uptake rhodamine 6G and TCPP according to the same procedure. After repeated wash, there was no color change.

Acid-base titration of UiO-66-150

The acid-base titration for UiO-66-150 was operated according to the reported method.^{3,4} Typically, 50

mg of the sample powder was loaded in a 100 mL beaker. Then, 50 mL 0.01 M NaNO₃ solution was added and allowed to equilibrate for 18 h. Before titration, the pH was adjusted to 3.00 with 0.1 M HCl solution and then titrated with 0.1 M NaOH solution to a pH of 10.5-11 using injection volume of 0.020 mL and injection rate of 0.02 mL/min. Equivalence points were obtained from the first derivative of the resulting titration curve of pH as a function of NaOH solution volume. The defect sites were calculated according to the amount of NaOH solution used.

Catalytic acetalization reaction of furfural and methanol

The reaction was carried out in 20 mL vial with magnetic stirrer. In a typical reaction, furfural (1 mmol), 10 mg of UiO-66 as catalyst and 2 mL methanol as solvents were loaded in the vial. Anisole was added as internal standard. The reaction was proceeded under room temperature. Every 10 minutes, the reaction solution was examined using GC-MS to determine the conversion of furfural. For the reuse of catalyst, UiO-66 was washed using methanol for several times and used directly for the next cycle of reaction.

1.3 Analytical techniques

UV-Vis spectra were measured on a Thermo Scientific Evolution 300 UV/Visible spectrophotometer. FTIR spectra were obtained on a Thermo Scientific Nicolet™ iS™ 10 spectrometer. ¹H NMR spectra were obtained using a Varian 400-MR NMR spectrometer. Thermogravimetric analysis (TGA) data were collected on Mettler-Toledo TGA-DSC-1 with heating rate 5 °C/min from 30 °C to 750 °C under N₂ atmosphere. N₂ adsorption data were collected on a Micrometrics ASAP 2020 Plus accelerated surface area and porosimetry system at 77 K surface area and pore size analyzer. Samples were activated under vacuum at 150 °C for 12h with the activation port equipped on ASAP 2020. Powder X-ray diffraction (PXRD) patterns were collected on Rigaku Miniflex 600 using Cu K α radiation. Particle size was calculated from the PXRD pattern using Scherrer's equation.

$$D = \frac{K\lambda}{\beta\cos\theta}$$

D: the mean size of the crystalline

K: the dimensionless shape factor

λ : the X-ray wavelength

β : the line broadening at half the maximum intensity

θ : the Bragg angle.

The acetalization reaction of furfural with methanol was examined and identified using GCMS-QP2010 SE with DB-5 ms column from Shimadzu. TEM images were obtained with a Philips TEM microscope at 200 kV. Dynamic light scattering (DLS) was examined using Zetasizer Ver. 7.10 from Malvern Instrument.

2. XRD patterns of the UiO-66 samples with different precursor ratios

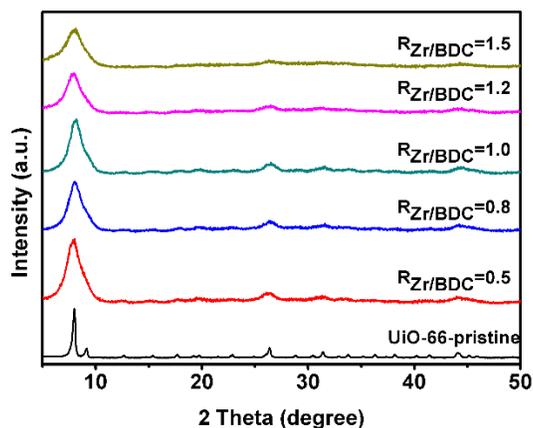


Fig. S1 XRD patterns of the UiO-66 samples with different precursor ratios

3. N₂ sorption isotherm of UiO-66 with R_{Zr}/BDC=1.5

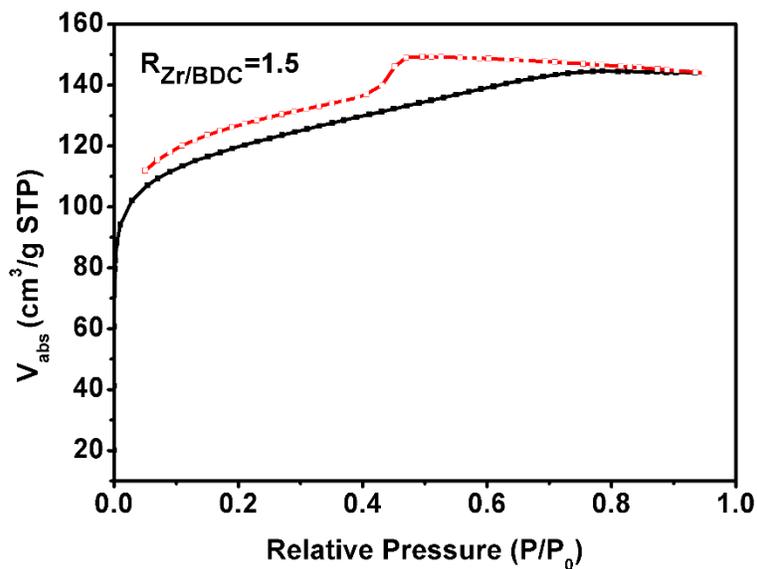


Fig. S2 N₂ sorption isotherm of UiO-66 with R_{Zr}/BDC=1.5

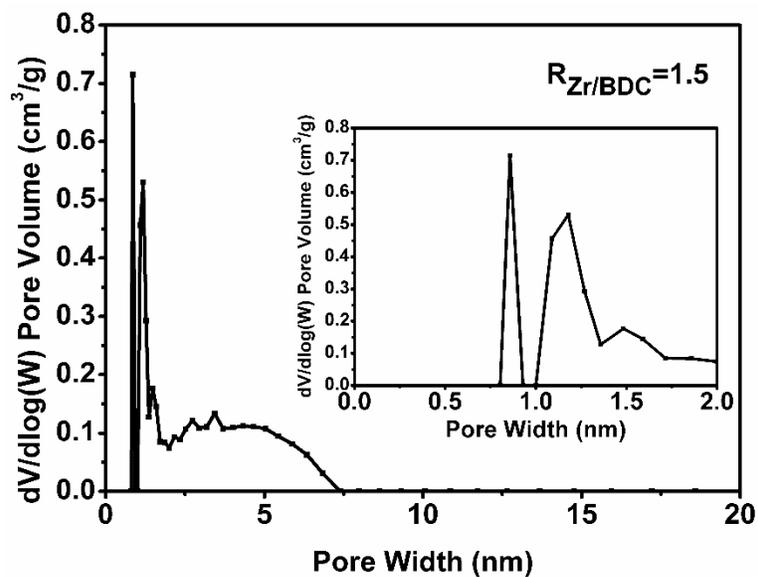


Fig. S3 Pore size distribution of UiO-66 with $R_{Zr/BDC}=1.5$

4. FT-IR spectra of UiO-66

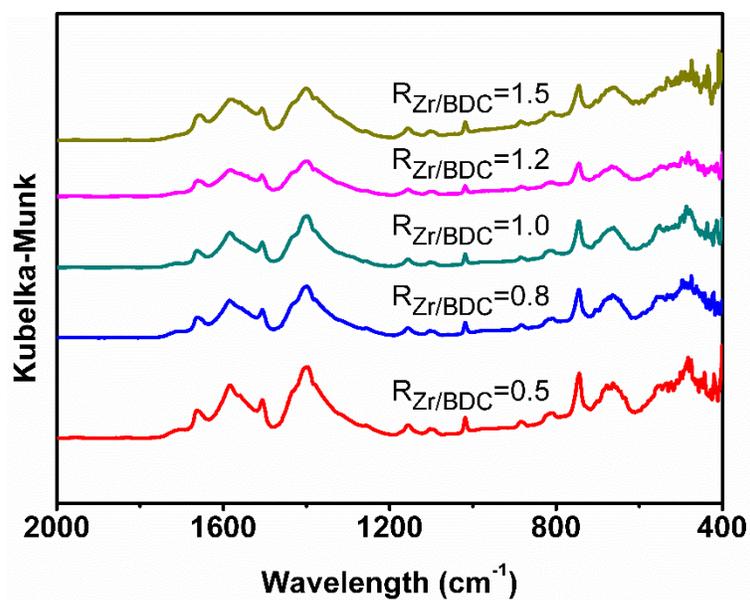


Fig. S4 FT-IR spectra of UiO-66 samples with different precursor ratios

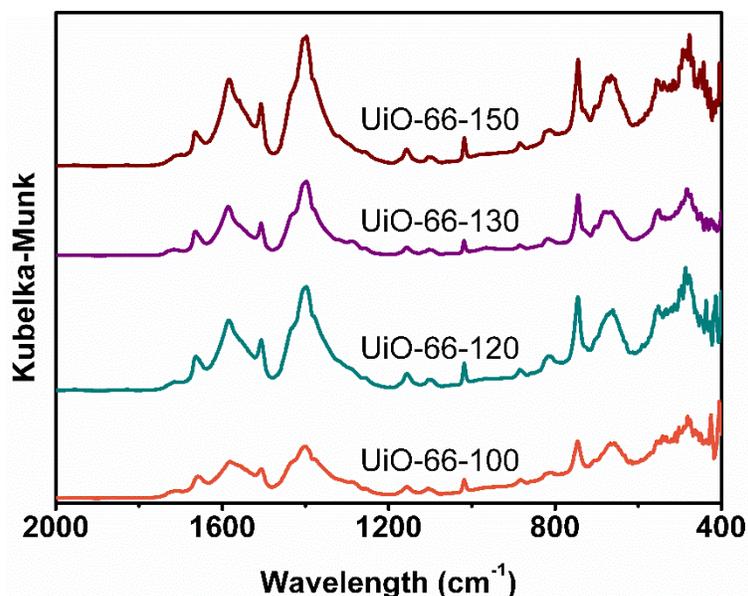


Fig. S5 FT-IR spectra of UiO-66 samples with different synthesis temperature

5. Porosity properties of UiO-66 samples with different precursor ratios and reaction temperatures

Table S1. Porosity property of UiO-66 with different precursor ratios

$R_{Zr/BDC}$	S_{BET}^a (m ² /g)	V_t^b (cm ³ /g)	V_{meso}^c/V_t
0.5	621	0.32	0.45
0.8	699	0.42	0.57
1.0	916	0.75	0.77
1.2	565	0.31	0.50
1.5	433	0.22	0.42

^a S_{BET} is the BET surface area. ^b V_t stands for the total pore volume determined by using the adsorption branch of the N₂ isotherm at $P/P_0=0.95$. ^c V_{meso} stands for the mesopore volume obtained from the BJH adsorption cumulative volume.

Table S2. Porosity property of UiO-66 with different synthesis temperatures

Temperature (°C)	S_{BET}^a (m ² /g)	V_t^b (cm ³ /g)	V_{meso}^c/V_t
100	836	0.51	0.60
120	916	0.75	0.77
130	887	0.72	0.78
150	1002	0.91	0.81

^a S_{BET} is the BET surface area. ^b V_t stands for the total pore volume determined by using the adsorption branch of the N₂ isotherm at $P/P_0=0.95$. ^c V_{meso} stands for the mesopore volume obtained from the BJH adsorption cumulative volume.

6. TEM images of UiO-66-150

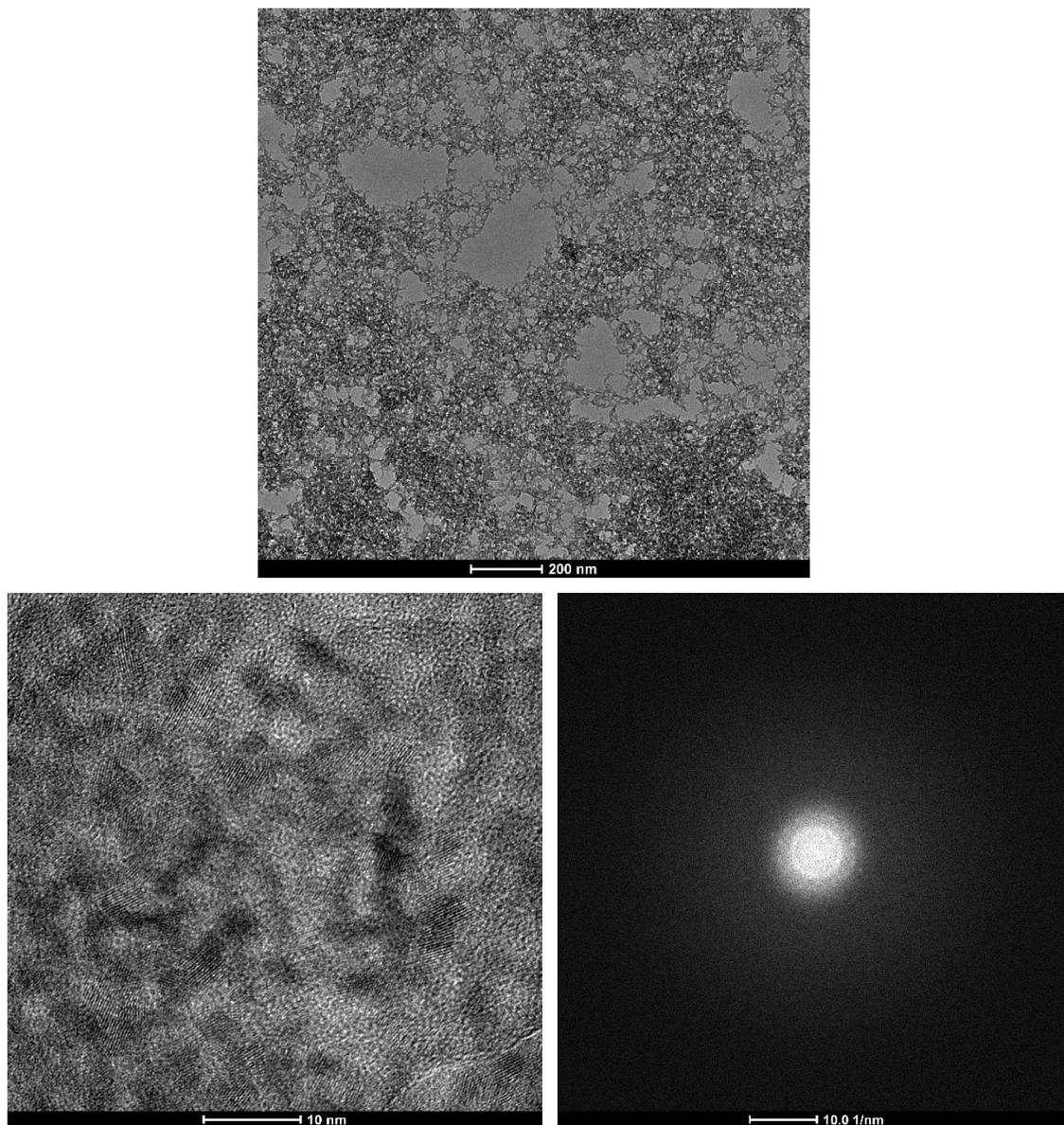


Fig. S6 TEM and HRTEM images of UiO-66-150 and the FFT pattern

7. DLS analysis of UiO-66-150

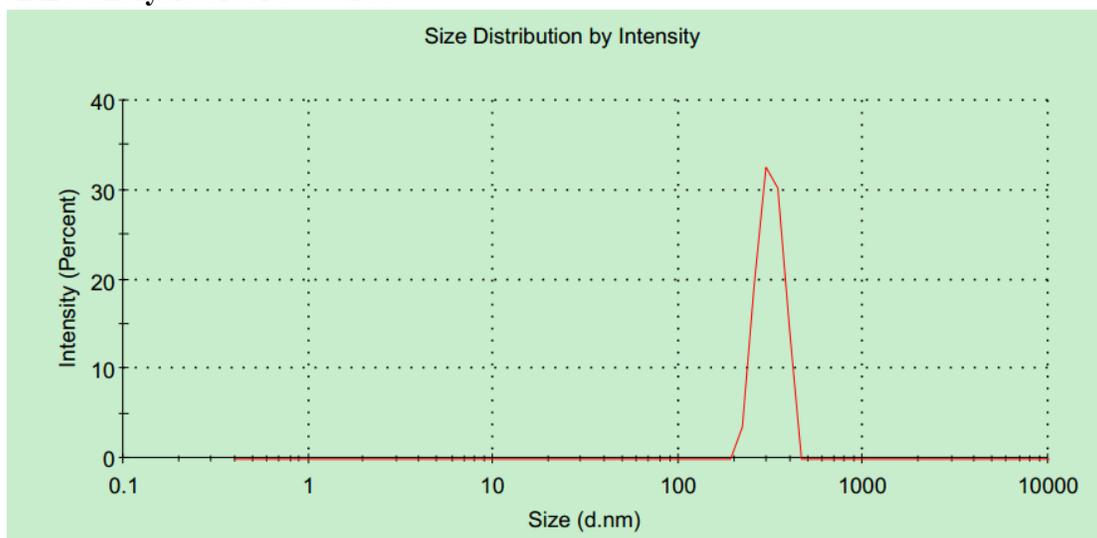


Fig.S7 Size distribution of UiO-66-150 tested through DLS

8. TG measurements of UiO-66 samples

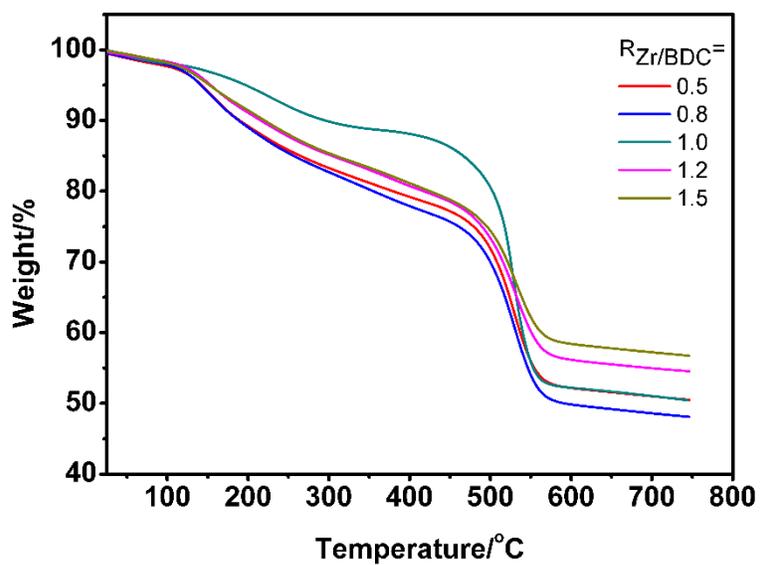


Fig. S8 TG curves of UiO-66 samples with different precursor ratios

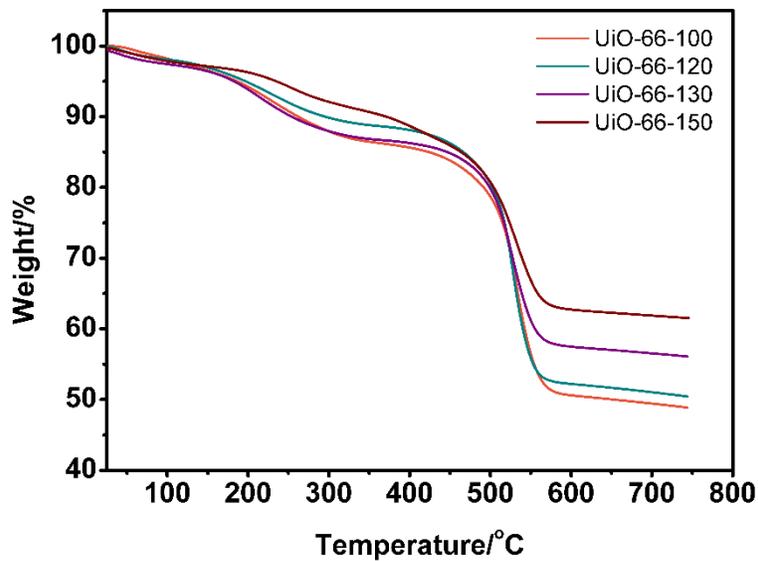


Fig. S9 TG curves of UiO-66 samples with different synthesis temperatures

9. FT-IR spectra of UiO-66-150-porphyrin

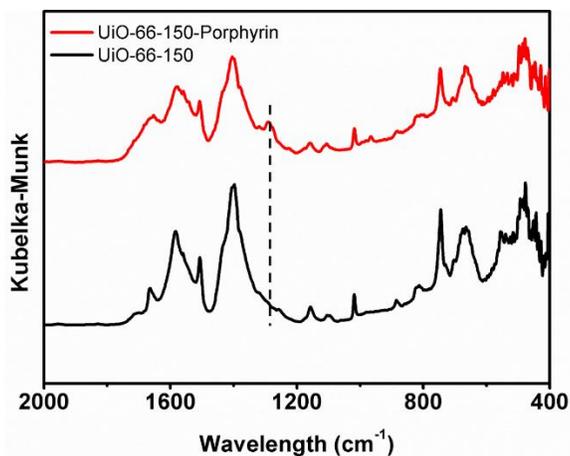


Fig. S10 FT-IR spectra of UiO-66-150 and UiO-66-150-porphyrin

10. ^1H NMR spectrum of UiO-66-150-porphyrin

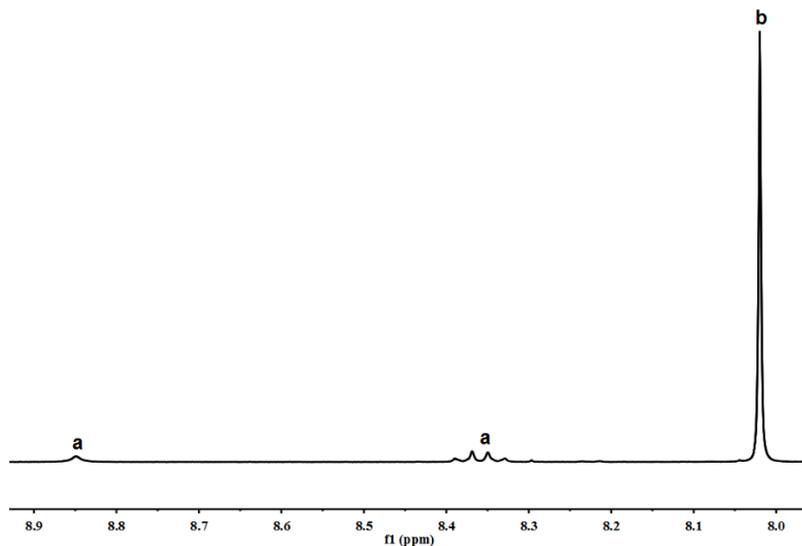


Fig. S11 Solution ^1H NMR spectrum of digested UiO-66-150-porphyrin. Peak a was assigned to TCPP and b was assigned to H_2BDC . The digest procedure: 15 mg of UiO-66-150-porphyrin was digested in 4 mL 37% HCl solution under heat. The dried product was dissolved in DMSO-d_6 for ^1H NMR test

11. N_2 sorption isotherm of UiO-66-150-porphyrin

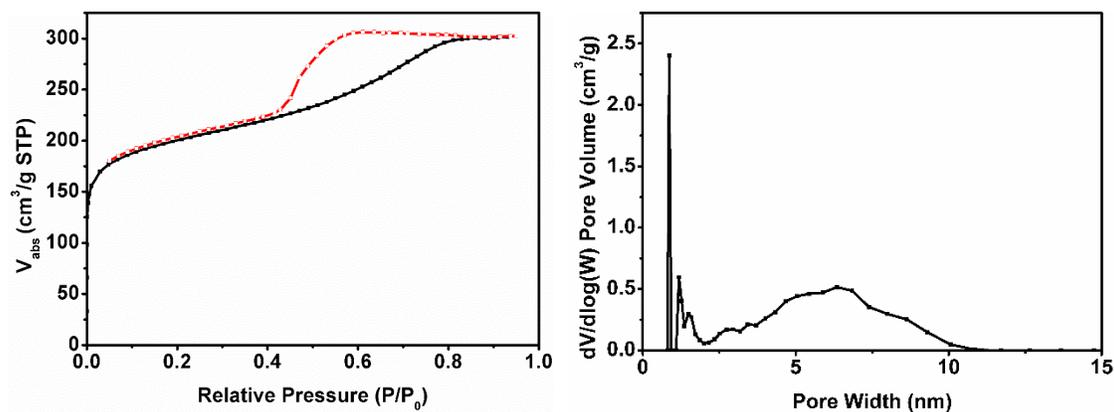


Fig. S12 N_2 sorption isotherm and pore size distribution of UiO-66-150-porphyrin. The BET surface area is $709 \text{ m}^2/\text{g}$.

12. TG measurement of UiO-66-150-porphyrin

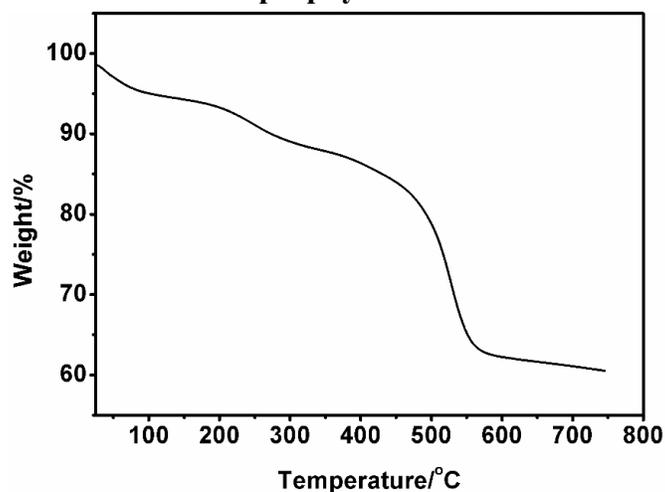


Fig. S13 TG curve of UiO-66-150-porphyrin

13. Acid-base titration of UiO-66-150

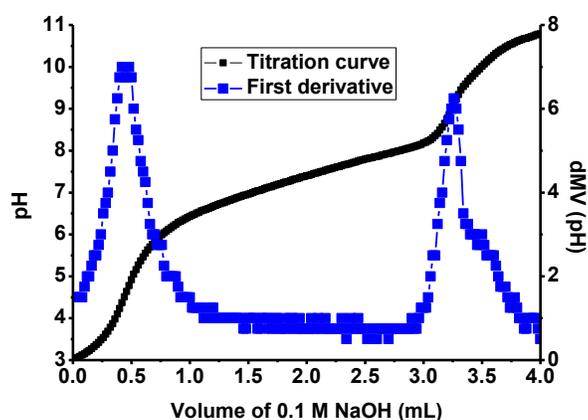
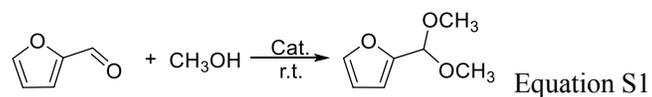


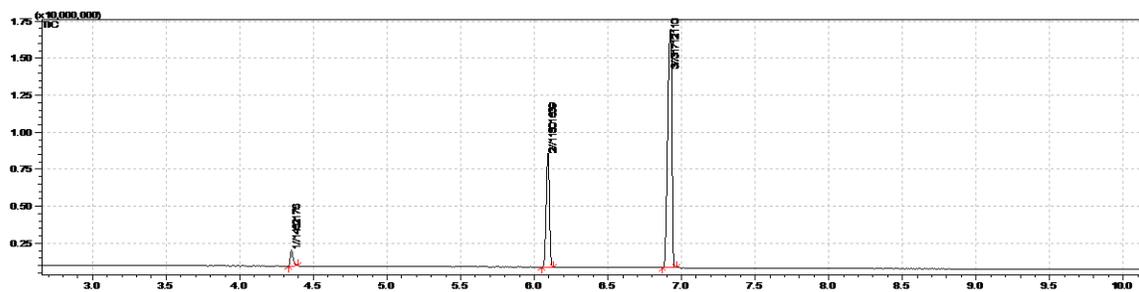
Fig. S14 Acid-base titration curve of UiO-66-150 and the first derivative curve

14. GC-MS spectra of the acetalization reaction

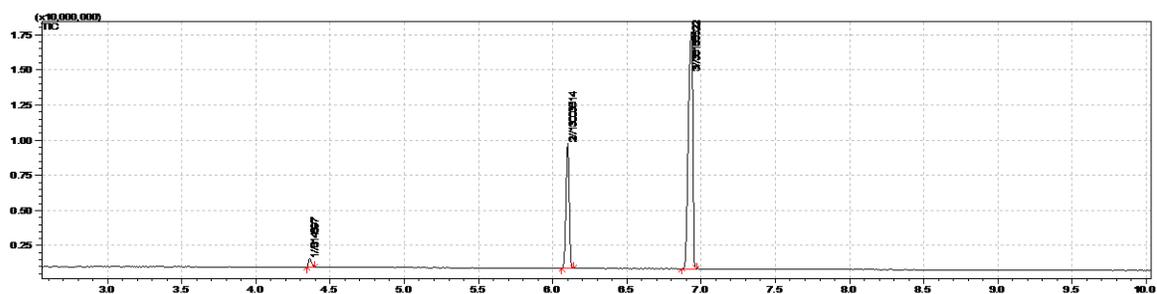


a) UiO-66-150 as catalyst. After reaction for 10, 20, 30, 40, 50, 60 minutes. The peaks from left to right refer to furfural, anisole as internal standard and the product.

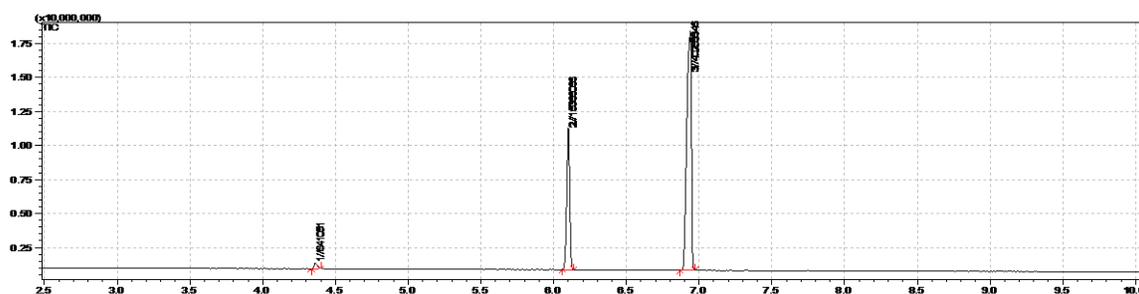
After reaction for 10 minutes



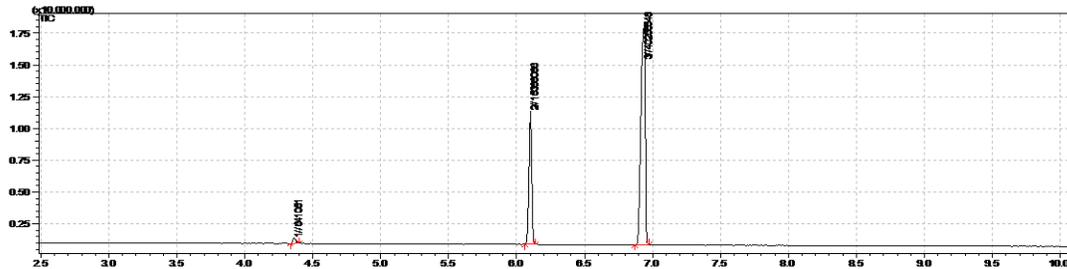
After reaction for 20 minutes



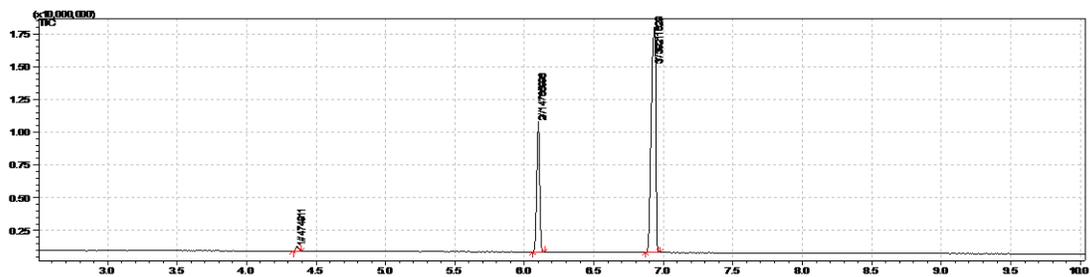
After reaction for 30 minutes



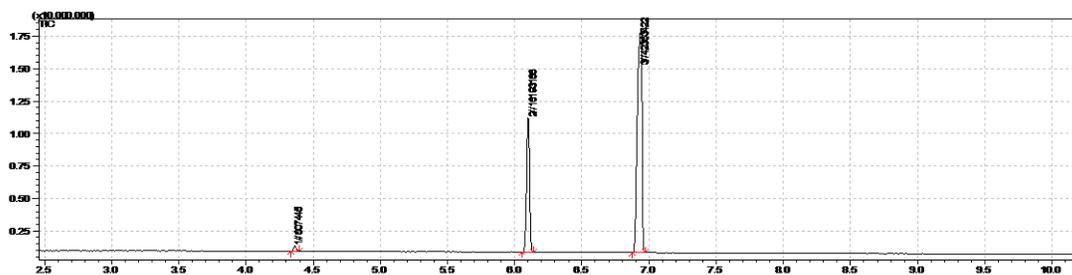
After reaction for 40 minutes



After reaction for 50 minutes

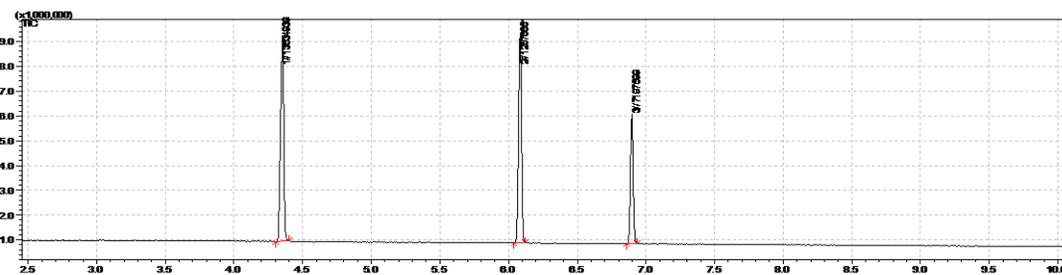


After reaction for 60 minutes

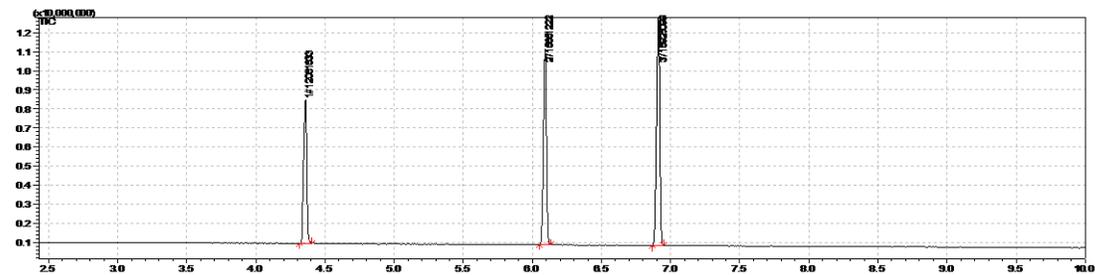


b) microporous UiO-66 as catalyst. After reaction for 10, 20, 30, 40, 50, 60 minutes. The peaks from left to right refer to furfural, anisole as internal standard and the product.

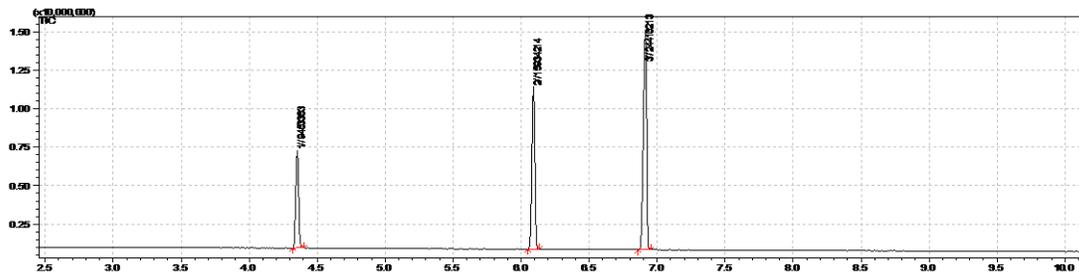
After reaction for 10 minutes



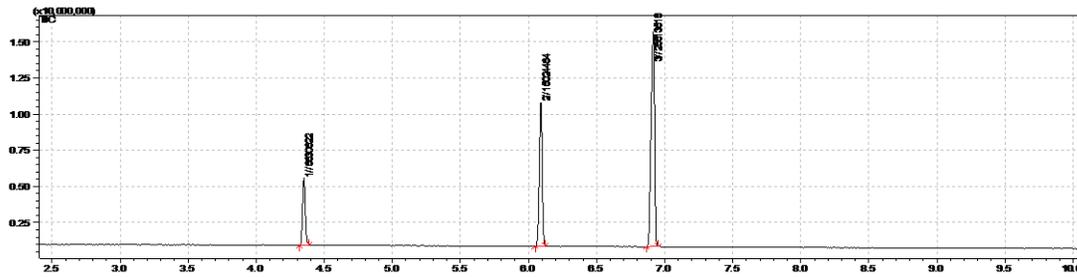
After reaction for 20 minutes



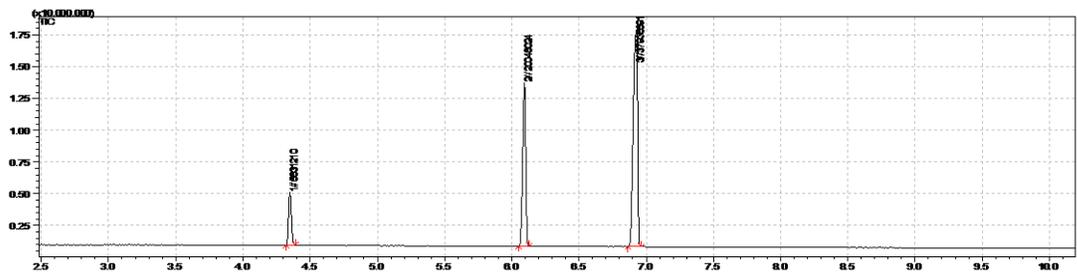
After reaction for 30 minutes



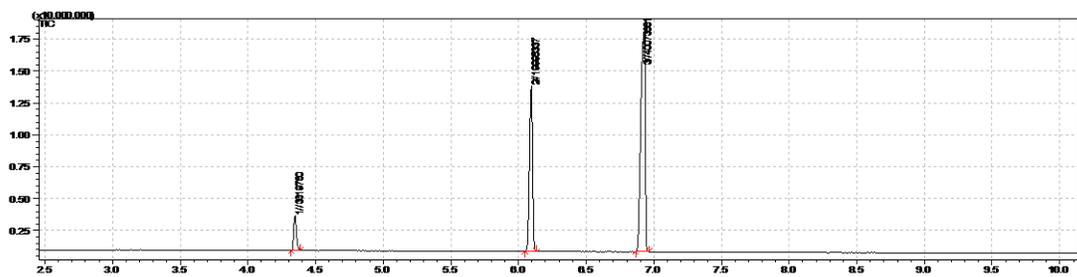
After reaction for 40 minutes



After reaction for 50 minutes



After reaction for 60 minutes



15. N₂ sorption isotherm of UiO-66-150 after reuse

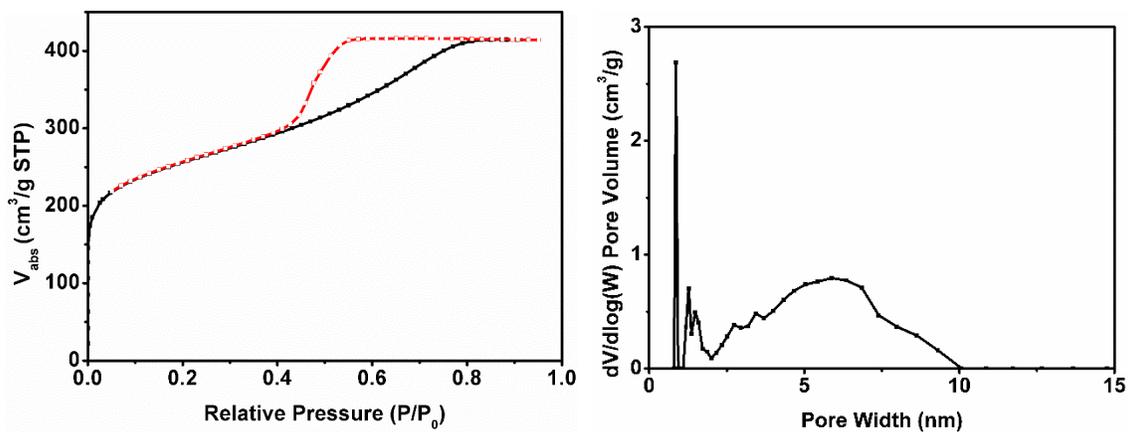


Fig. S15 N₂ sorption isotherm and pore size distribution of UiO-66-150 after reused for 5 times

16. N₂ sorption isotherms, BET linear report and pore size distribution of each UiO-66 sample

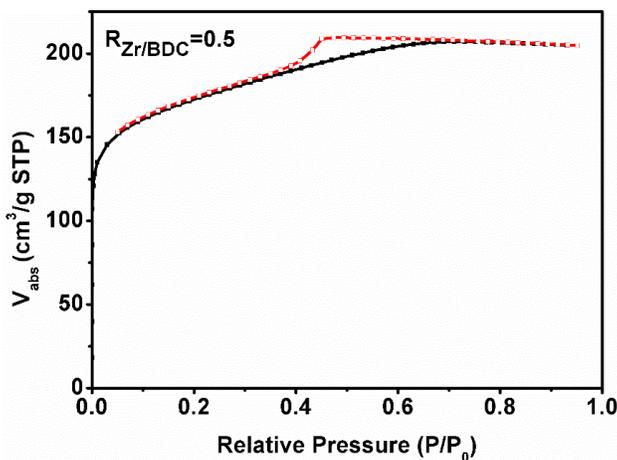


Fig. S16 N₂ sorption isotherm of R_{Zr/BDC}=0.5 at 77 K

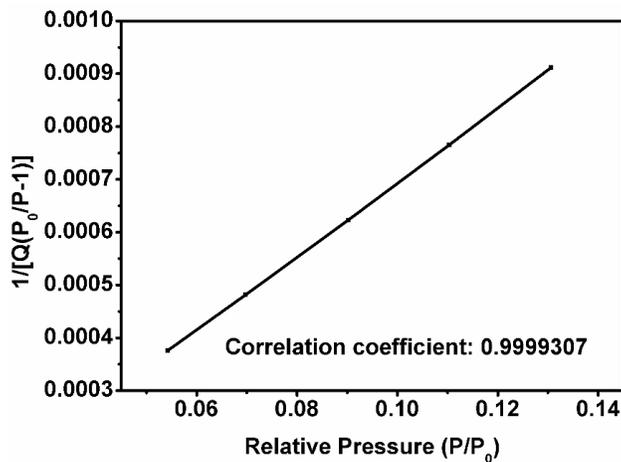


Fig. S17 BET plot from N₂ isotherm at 77 K of R_{Zr/BDC}=0.5

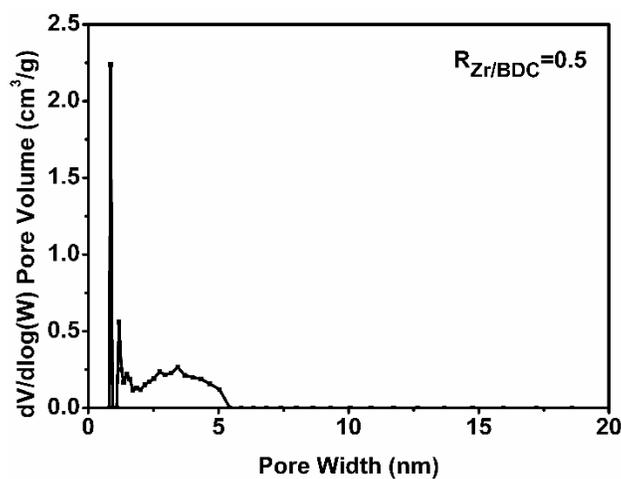


Fig. S18 DFT pore size distribution of R_{Zr/BDC}=0.5 measured with N₂ at 77 K

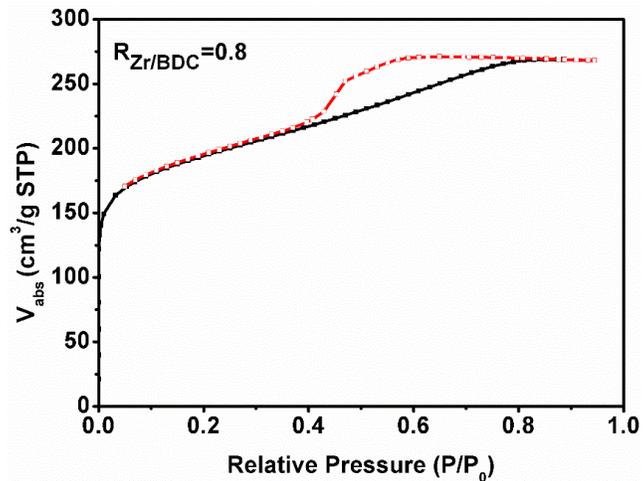


Fig. S19 N₂ sorption isotherm of R_{Zr/BDC}=0.8 at 77 K

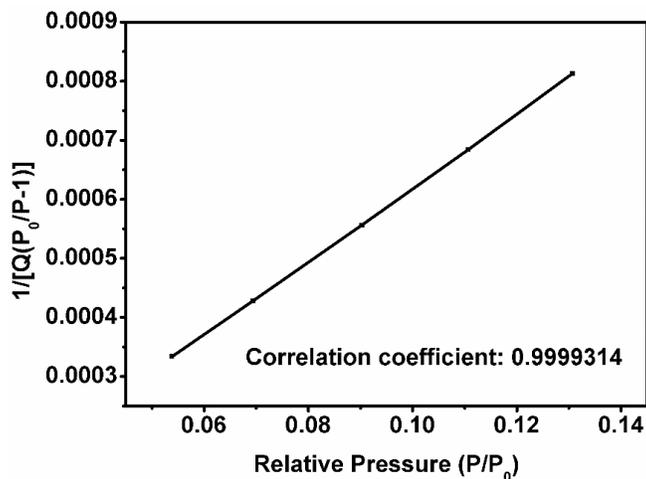


Fig. S20 BET plot from N₂ isotherm at 77 K of R_{Zr/BDC}=0.8

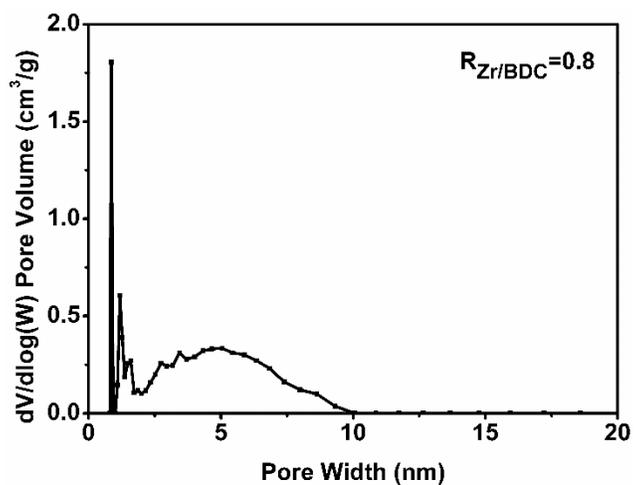


Fig. S21 DFT pore size distribution of R_{Zr/BDC}=0.8 measured with N₂ at 77 K

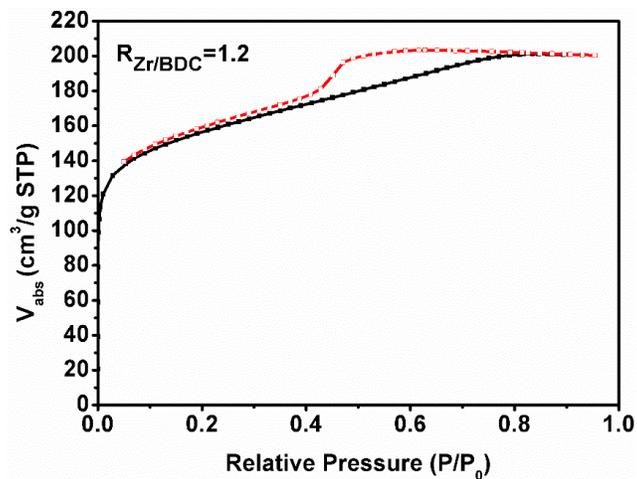


Fig. S22 N₂ sorption isotherm of R_{Zr/BDC}=1.2 at 77 K

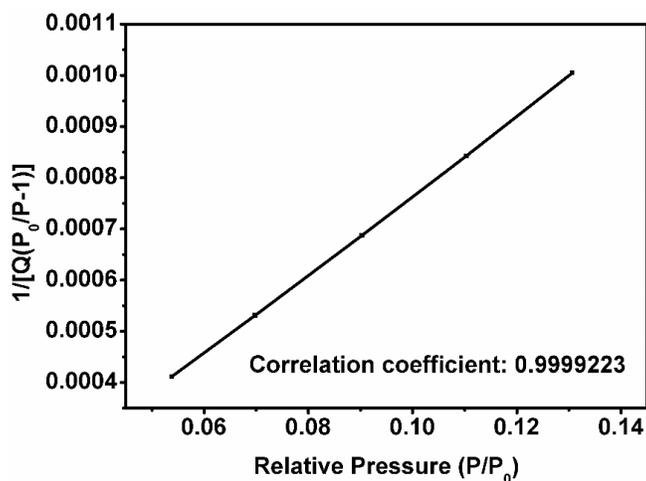


Fig. S23 BET plot from N₂ isotherm at 77 K of R_{Zr/BDC}=1.2

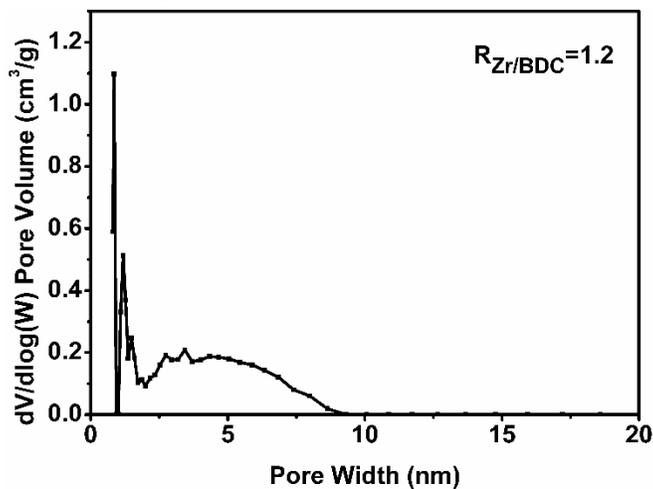


Fig. S24 DFT pore size distribution of R_{Zr/BDC}=1.2 measured with N₂ at 77 K

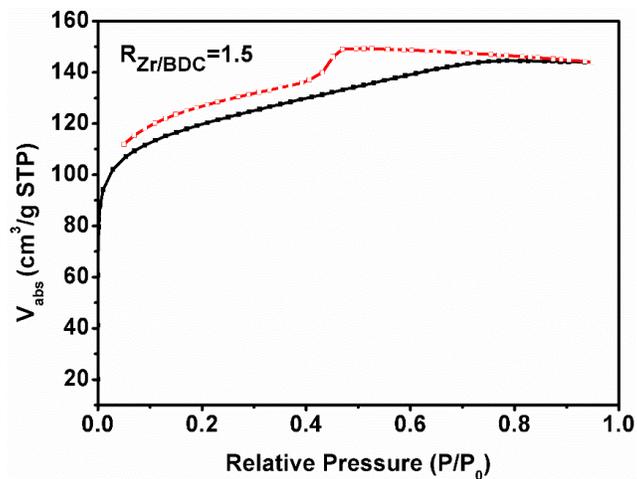


Fig. S25 N₂ sorption isotherm of R_{Zr/BDC}=1.5 at 77 K

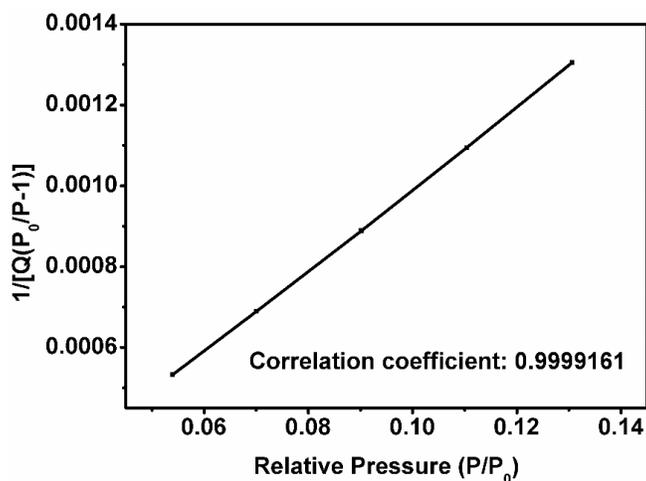


Fig. S26 BET plot from N₂ isotherm at 77 K of R_{Zr/BDC}=1.5

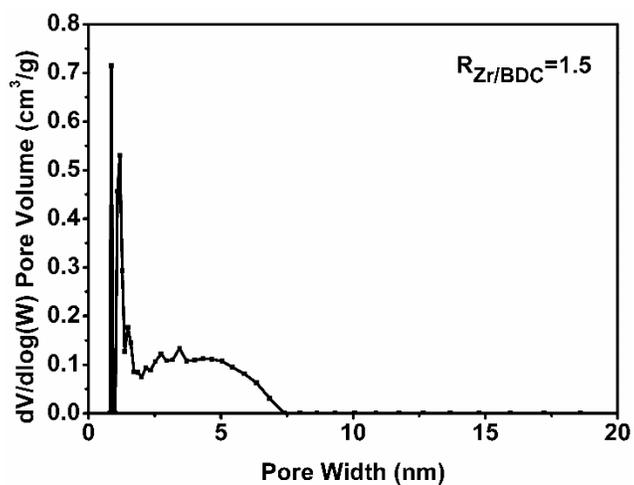


Fig. S27 DFT pore size distribution of R_{Zr/BDC}=1.5 measured with N₂ at 77 K

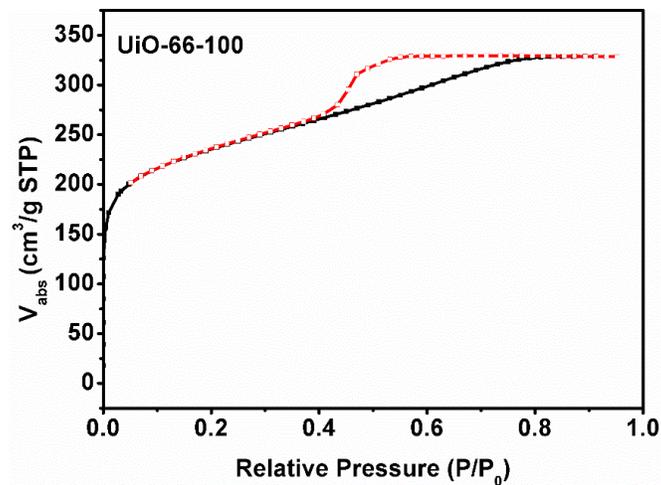


Fig. S28 N₂ sorption isotherm of UiO-66-100 at 77 K

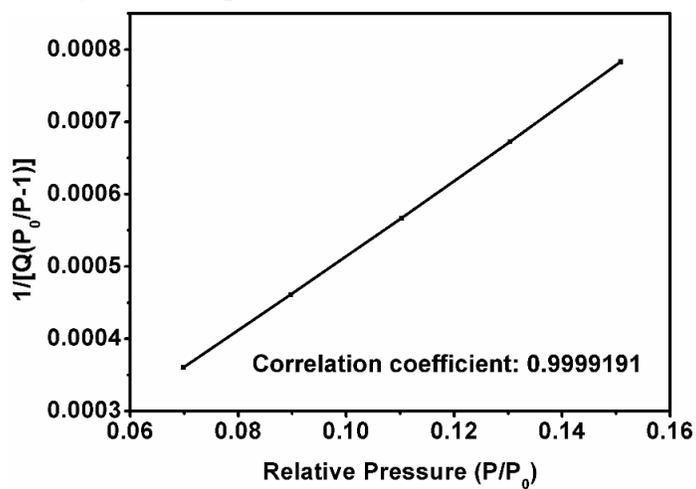


Fig. S29 BET plot from N₂ isotherm at 77 K of UiO-66-100

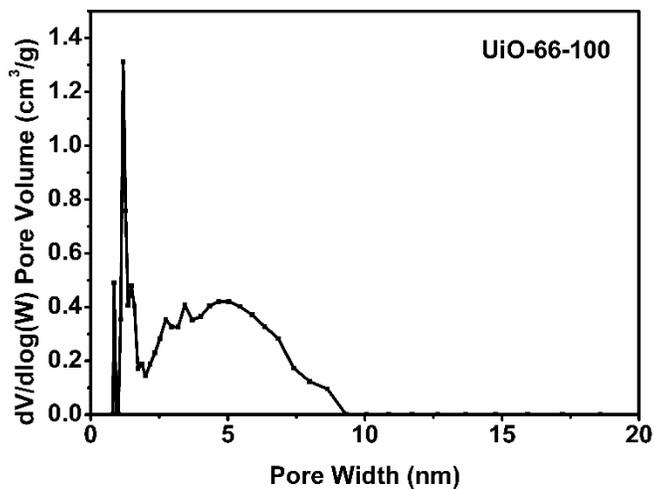


Fig. S30 DFT pore size distribution of UiO-66-100 measured with N₂ at 77 K

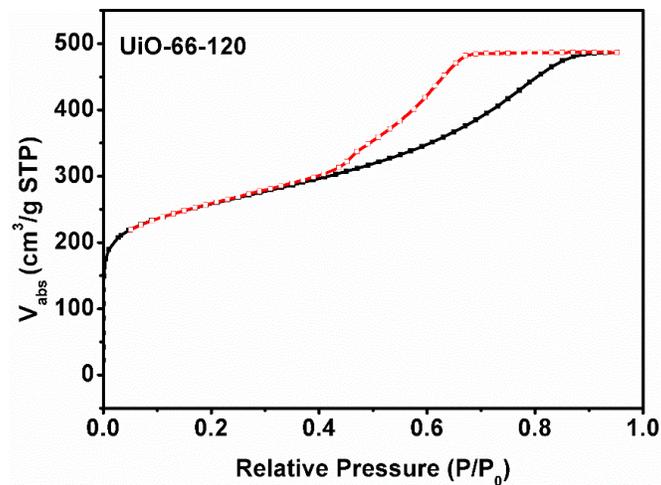


Fig. S31 N₂ sorption isotherm of UiO-66-120 at 77 K

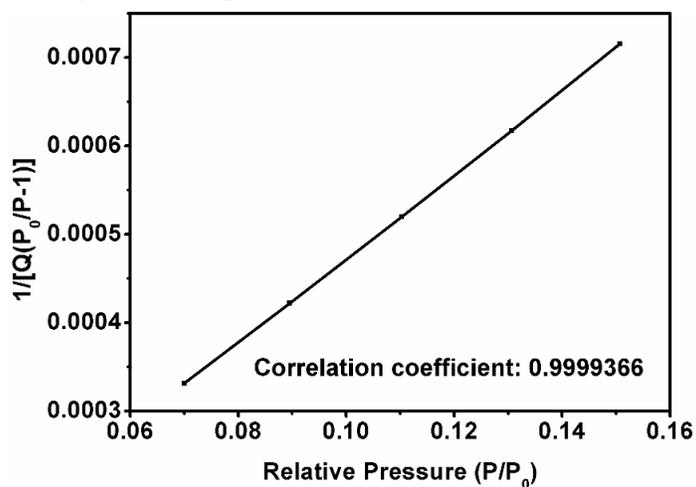


Fig. S32 BET plot from N₂ isotherm at 77 K of UiO-66-120

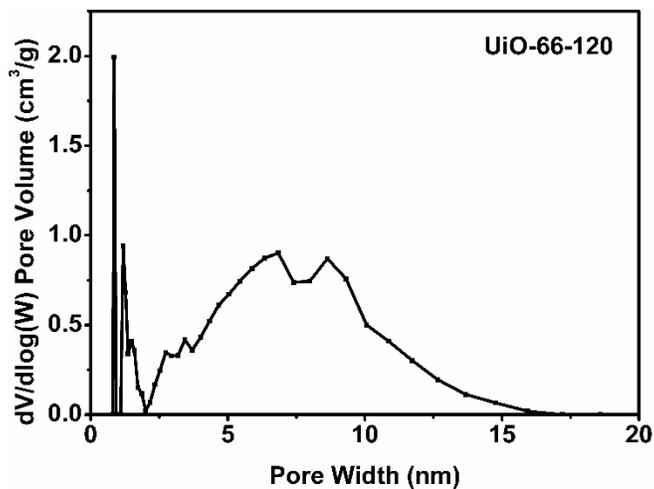


Fig. S33 DFT pore size distribution of UiO-66-120 measured with N₂ at 77 K

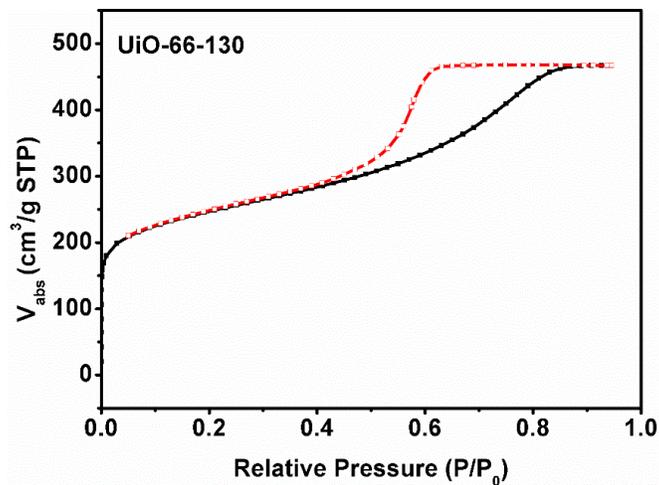


Fig. S34 N₂ sorption isotherm of UiO-66-130 at 77 K

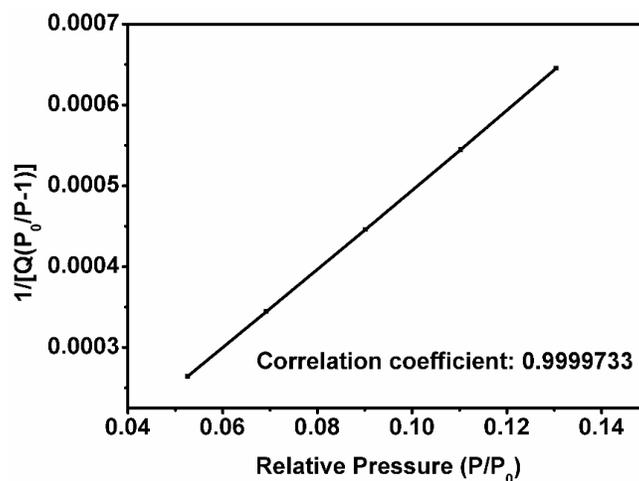


Fig. S35 BET plot from N₂ isotherm at 77 K of UiO-66-130

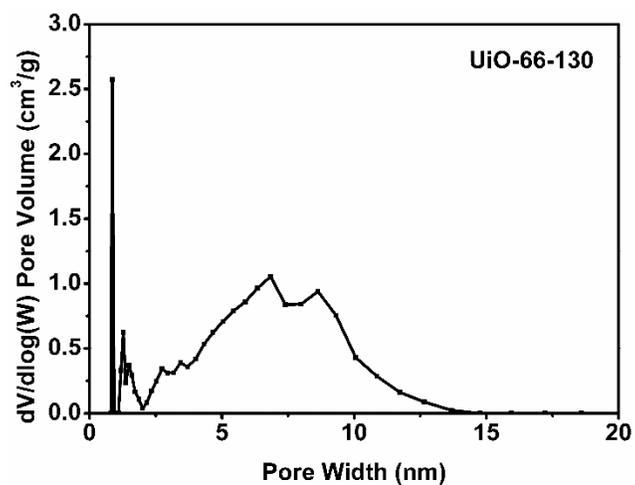


Fig. S36 DFT pore size distribution of UiO-66-130 measured with N₂ at 77 K

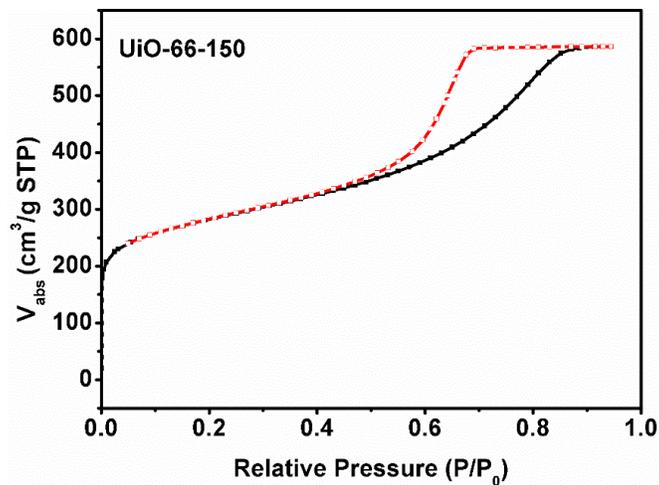


Fig. S37 N₂ sorption isotherm of UiO-66-150 at 77 K

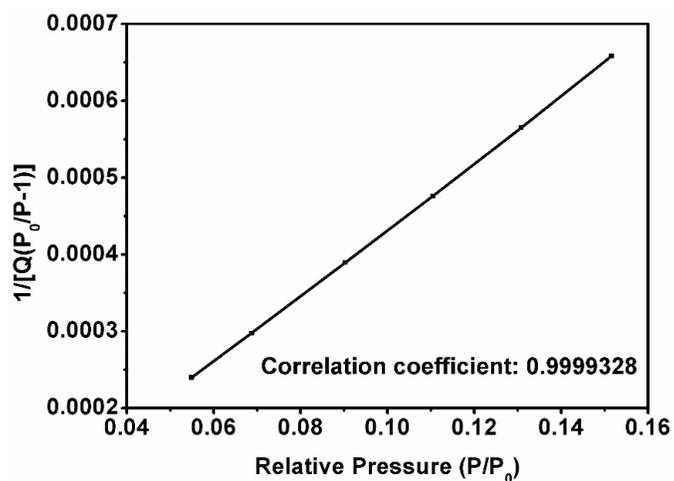


Fig. S38 BET plot from N₂ isotherm at 77 K of UiO-66-150

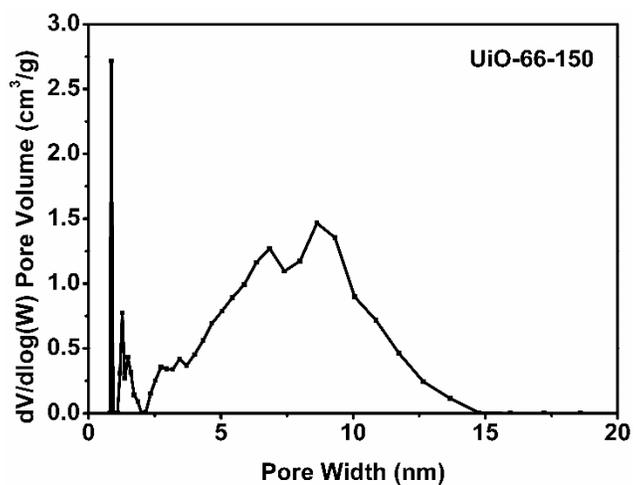


Fig. S39 DFT pore size distribution of UiO-66-150 measured with N₂ at 77 K

17. TG curve of each UiO-66 sample

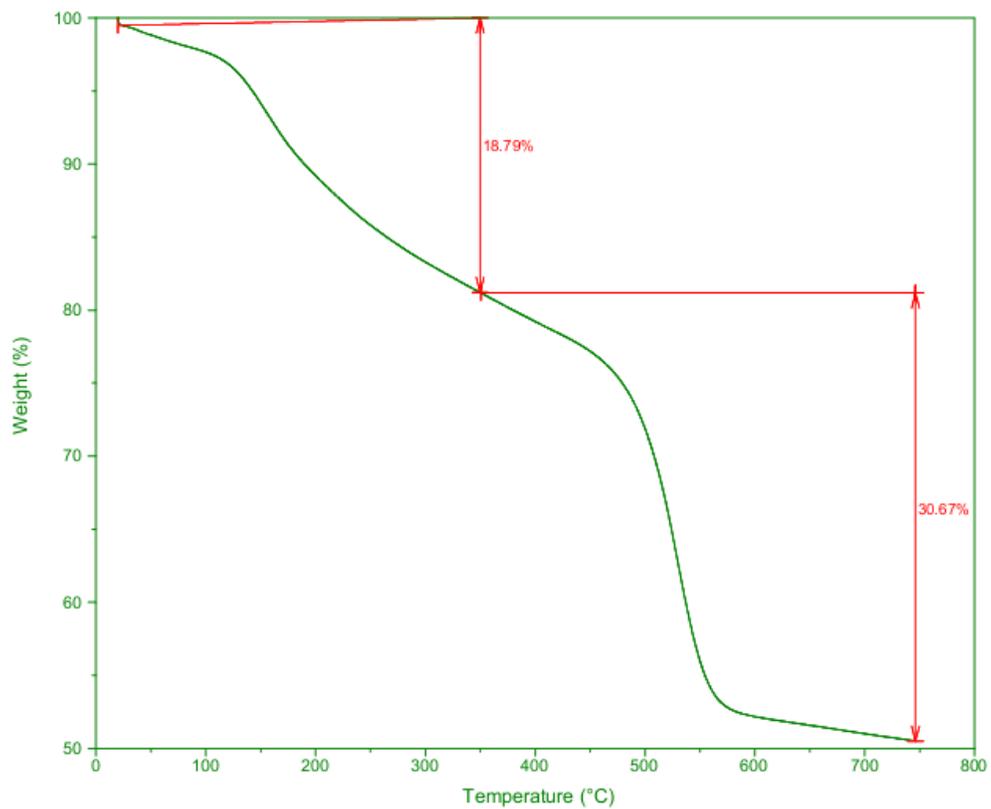


Fig. S40 TG analysis of $R_{Zr/BDC}=0.5$. Based on the calculated result, 18.79% weight loss is due to the trapped water and DMF molecules, and water molecules on the Zr_6 clusters (30-350 °C). The decomposition temperature is around 500 °C.

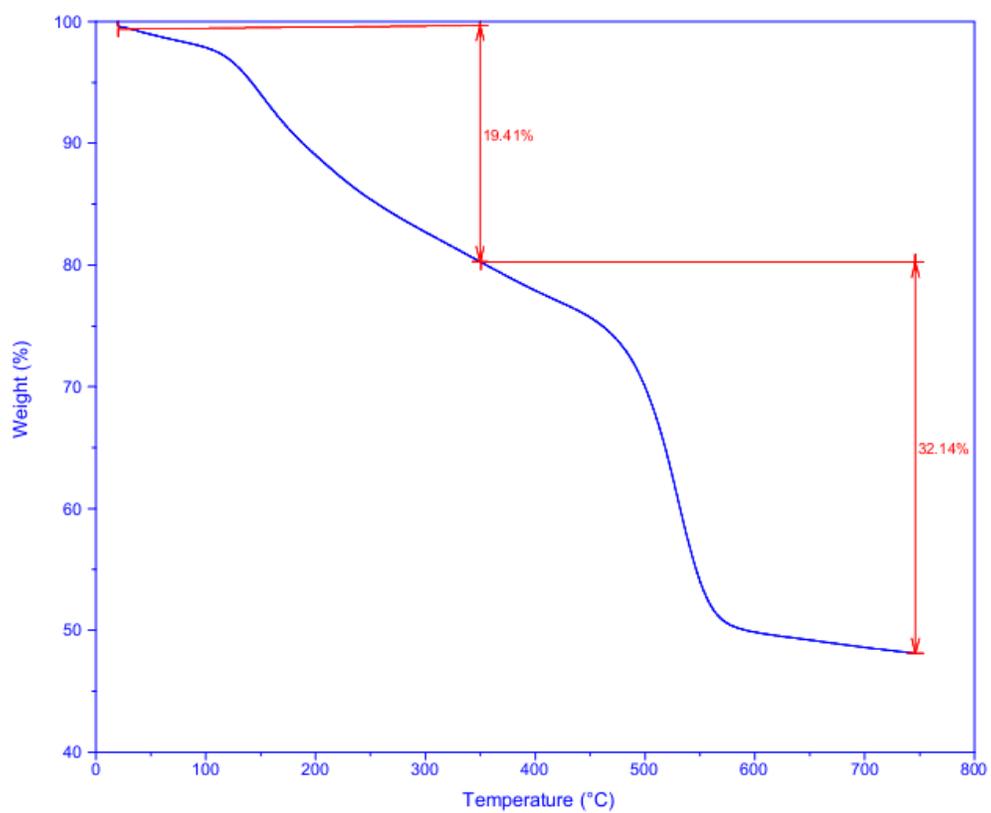


Fig. S41 TG analysis of $R_{Zr/BDC}=0.8$. Based on the calculated result, 19.41% weight loss is due to the trapped water and DMF molecules, and water molecules on the Zr_6 clusters (30-350 °C). The decomposition temperature is around 500 °C.

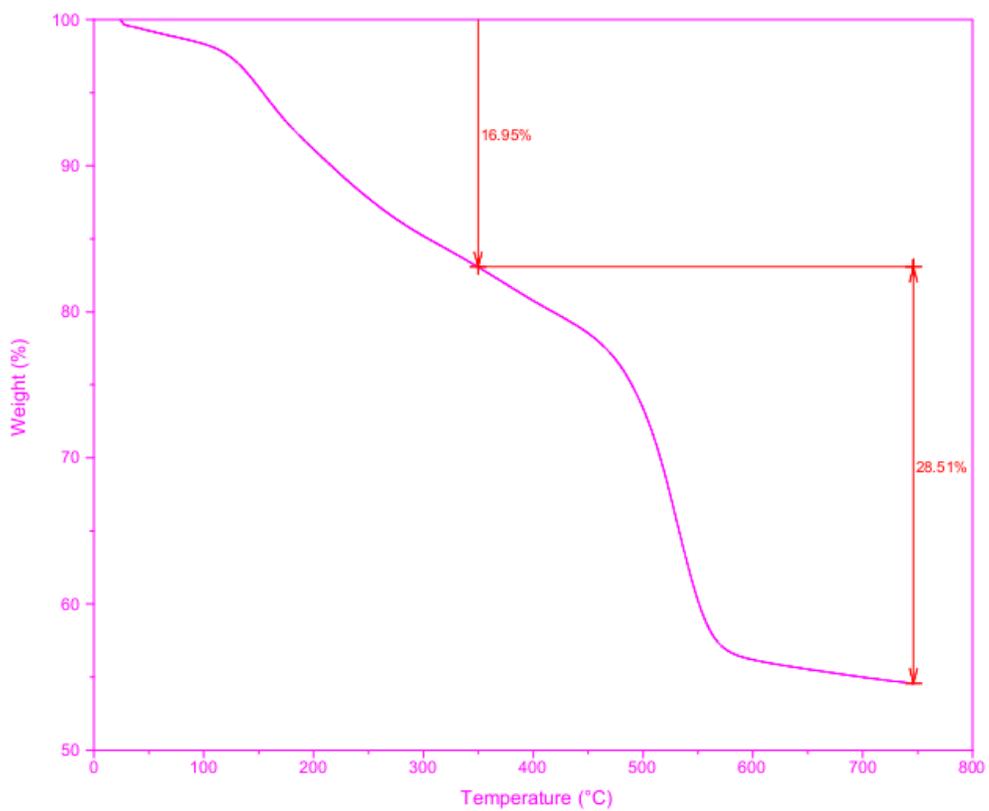


Fig. S42 TG analysis of $R_{Zr/BDC}=1.2$. Based on the calculated result, 16.95% weight loss is due to the trapped water and DMF molecules, and water molecules on the Zr_6 clusters (30-350 °C). The decomposition temperature is around 500 °C.

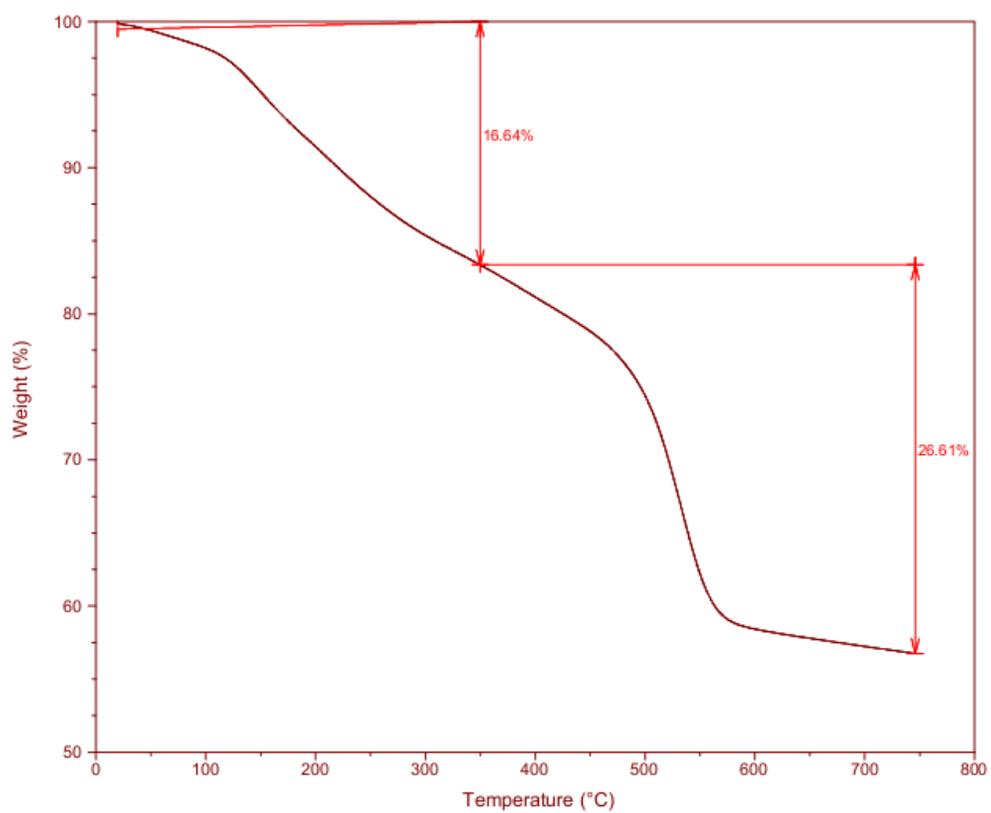


Fig. S43 TG analysis of $R_{Zr/BDC}=1.5$. Based on the calculated result, 16.64% weight loss is due to the trapped water and DMF molecules, and water molecules on the Zr_6 clusters (30-350 °C). The decomposition temperature is around 500 °C.

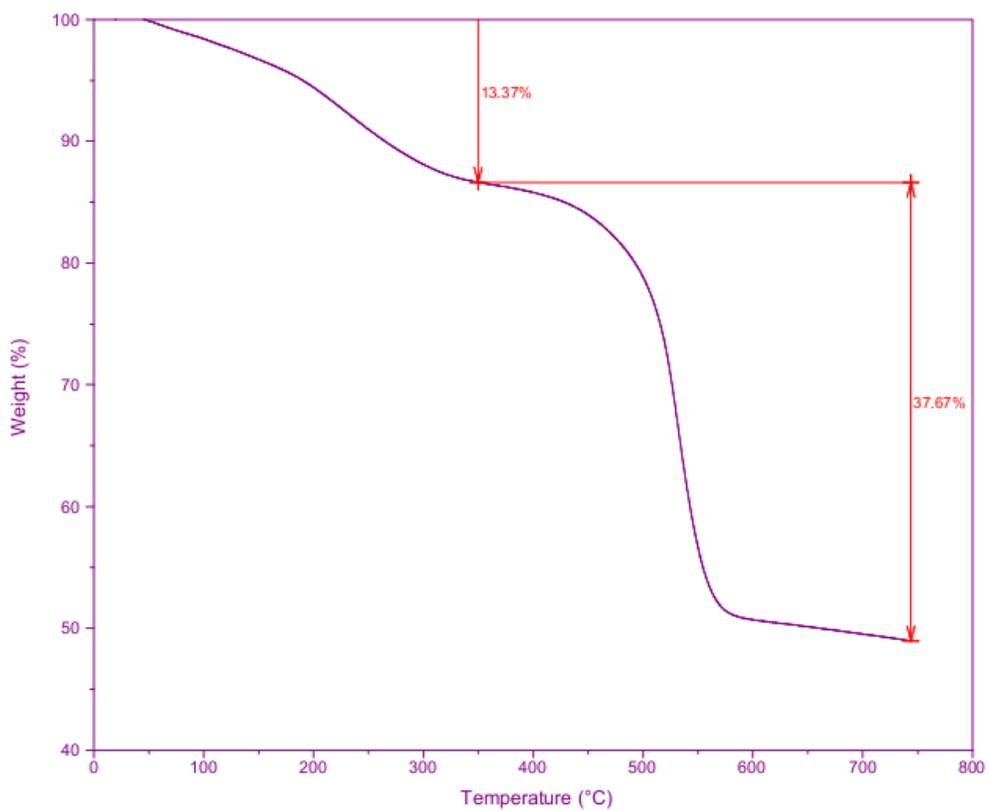


Fig. S44 TG analysis of UiO-66-100. Based on the calculated result, 13.37% weight loss is due to the trapped water and DMF molecules, and water molecules on the Zr_6 clusters (30-350 °C). The decomposition temperature is around 500 °C.

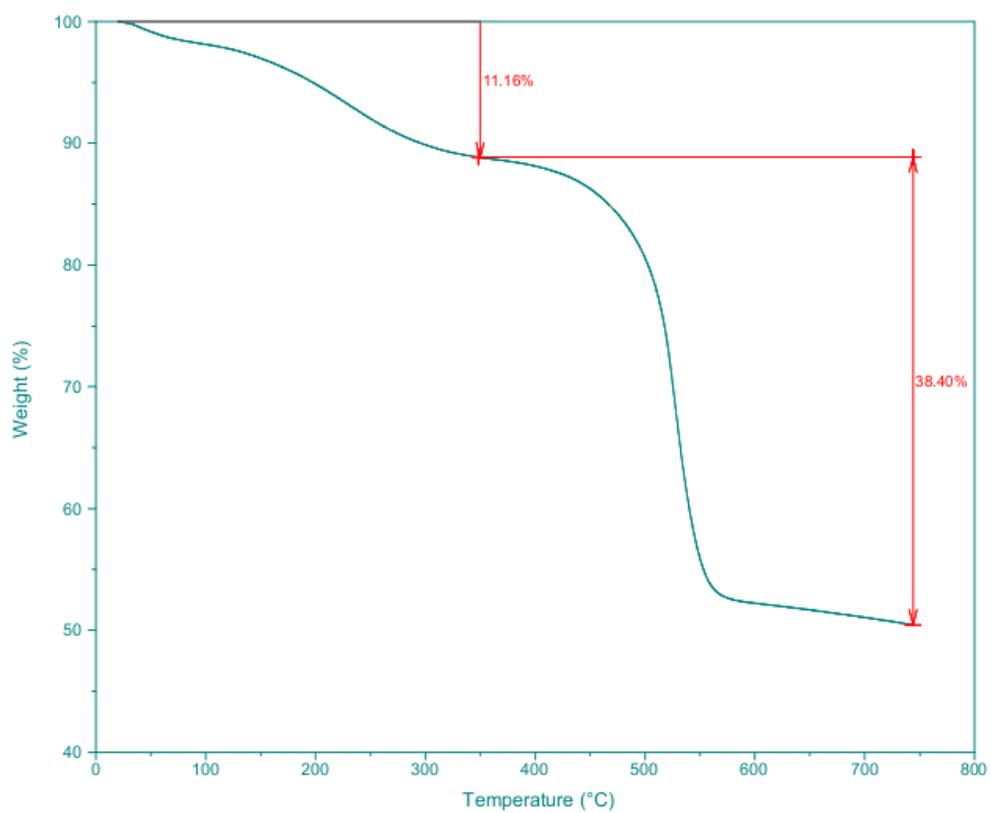


Fig. S45 TG analysis of UiO-66-120. Based on the calculated result, 11.16% weight loss is due to the trapped water and DMF molecules, and water molecules on the Zr_6 clusters (30-350 °C). The decomposition temperature is around 500 °C.

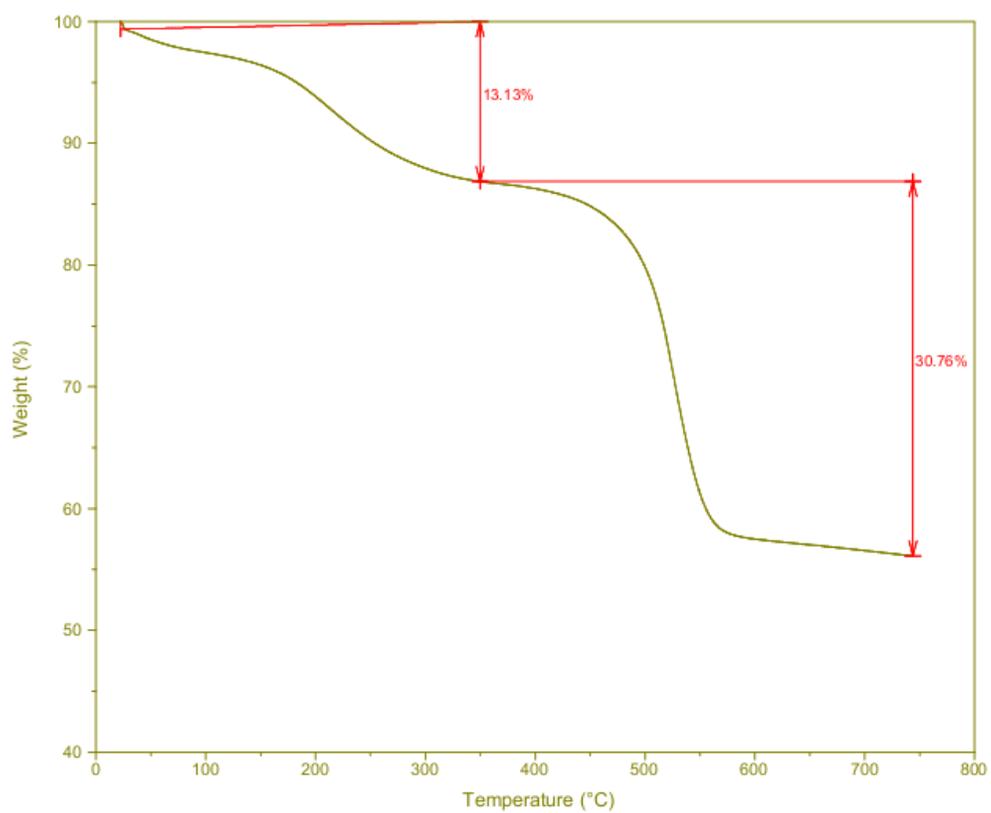


Fig. S46 TG analysis of UiO-66-130. Based on the calculated result, 13.13% weight loss is due to the trapped water and DMF molecules, and water molecules on the Zr_6 clusters (30-350 °C). The decomposition temperature is around 500 °C.

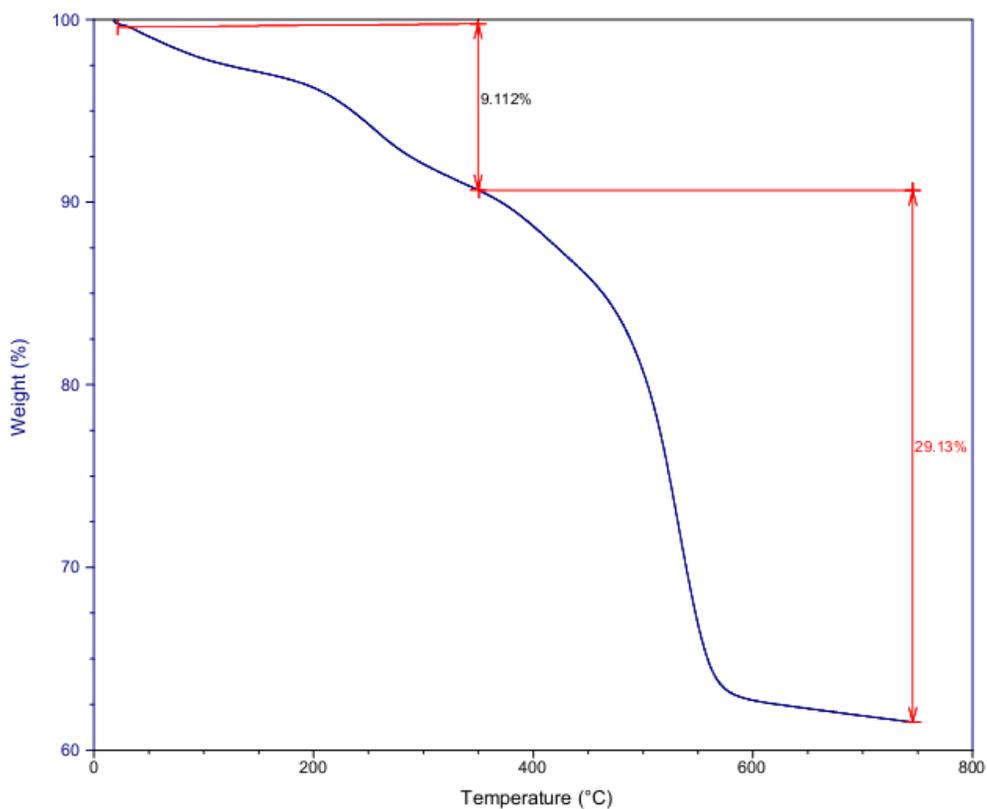


Fig. S47 TG analysis of UiO-66-150. Based on the calculated result, 9.112% weight loss is due to the trapped water and DMF molecules, and water molecules on the Zr_6 clusters (30-350 °C). The decomposition temperature is around 500 °C.

18. References

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