

## Supporting Information

### **Solid-phase rapid synthesis of hierarchical UiO-type metal-organic framework as excellent solid acid catalyst for acetalization of benzaldehyde with alcohol**

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## 1.1. Materials

Zirconium oxychloride octahydrate ( $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ ), 2,5-dihydroxyterephthalic acid ( $\text{BDC}-(\text{OH})_2$ ), zirconium tetrachloride ( $\text{ZrCl}_4$ ), benzaldehyde, methanol, ethanol, *n*-propanol, *n*-butanol, and *N,N*-dimethylformamide (DMF) were purchased from Aladdin Biochemical Technology Co., Ltd. All chemicals were analytically pure and used without further purification.

## 1.2 Characterization

Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku D/Max-2550 diffractometer equipped with a SolX Detector-Cu  $\text{K}\alpha$  radiation with wavelength of  $\lambda = 1.5418 \text{ \AA}$ . Scanning electron microscopy (SEM) images were recorded on SUPRA 55 operated with an acceleration voltage of 15 kV. Nitrogen sorption isotherms were obtained at 77 K on a BSD-PS1 gas sorption and porosimetry system (The samples were normally degassed at 423 K under vacuum until a final pressure of  $1 \times 10^{-3}$  Torr was reached prior to the measurement). Transmission electron microscope (TEM) and high-resolution transmission electron microscopy (HR-TEM) images were acquired with a FEI Tecnai G2 F30 operated at 300 kV with an energy-dispersive X-ray (EDX) spectrometer. Elemental analysis was performed on Vario EL III from Elementar. Fourier transform infrared (FT-IR) spectra were recorded on a NicoLET iS10 spectrometer. Thermogravimetric analysis was carried out on TGA Q500. X-ray photoelectron spectroscopy (XPS) was performed on an Axis ultra DLD (Kratos analytical) with a monochromatic Al  $\text{K}\alpha$  X-ray source ( $h\nu = 1486.6 \text{ eV}$ ). UV-visible diffuse reflectance spectra were recorded on a UV-2500 scanning spectrophotometer (Shimadzu). Zr contents were determined with an iCAP 7600 ICP-OES analyzer calibrated with standard solutions.

### 2.1. Solid-phase synthesis of UiO-66(Zr)-(OH)<sub>2</sub>:

2 mmol  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  (644.5 mg) and 1.75 mmol  $\text{BDC}-(\text{OH})_2$  (346.7 mg) were mixed in a mortar and ground by hand about 7 min under ambient condition. The mixtures were transferred into 20 mL Teflon-lined autoclave for crystallizing at certain temperature for certain time in a pre-heated oven. When the reaction time is reached, the autoclave is taken out the oven and cooled to ambient temperature. The obtained solids were respectively washed with 25 mL ethanol, 50 mL ethanol at 70 °C for 4 h, and 25 mL ethanol to remove the unreacted reactants. Finally, the prepared samples

were dried and denoted as UiO-66(Zr)-(OH)<sub>2</sub>-X-Y (where X and Y represent the crystallization temperature and time during the synthesis process).

## **2.2. Solvothermal synthesis of UiO-66(Zr)-(OH)<sub>2</sub>:**

1.5 mmol ZrCl<sub>4</sub> (349.6 mg) and 1.25 mmol BDC-(OH)<sub>2</sub> (247.7 mg) were added into 30 mL DMF. After dissolving, the solution was transferred into 50 mL Teflon-lined autoclave and crystallized at 120 °C for 24 h in a pre-heated oven. After completely cooled, the final solid was respectively washed with 25 mL DMF, 50 mL ethanol at 70 °C for 4 h and 25 mL ethanol to remove the unreacted reactants. Finally, the prepared sample was dried and denoted as UiO-66(Zr)-(OH)<sub>2</sub>-solvent.

## **2.3. Solvothermal synthesis of defective UiO-66(Zr)-(OH)<sub>2</sub>-solvent:**

The defective UiO-66(Zr)-(OH)<sub>2</sub>-solvent was synthesized by solvothermal method with formic acid as modulator: 1.5 mmol ZrCl<sub>4</sub> (349.6 mg) and 1.5 mmol BDC-(OH)<sub>2</sub> (247.7 mg) were dissolved in 40 mL DMF. Then 11 mL formic acid was added to the mixture, and the mixture was agitated in the sonicator for around 10 min. The mixture was transferred into 100 mL Teflon-lined autoclave and crystallized at 120 °C for 21 h in a pre-heated oven. After completely cooled, the final solid was respectively washed with 30 mL DMF, 50 mL ethanol at 70 °C for 4 h and 30 mL ethanol to remove the unreacted reactants. Finally, the prepared sample was dried and denoted as defective UiO-66(Zr)-(OH)<sub>2</sub>-solvent.

## **3.1. Acetalization of benzaldehyde with methanol:**

Before testing, the catalysts were activated at 150 °C for 6 h. In a typical reaction, 20 mg catalyst was dispersed in 15 mL methanol in a 20 mL dram vial and immersed in water bath at 25 °C with a magnetic stirrer (800 rpm). The catalyst reaction was initiated by the addition of 6 mmol benzaldehyde. Liquid samples were withdrawn at regular intervals by disposable syringe, and filtered with the 0.22 μm syringe filter, and analyzed by gas chromatography on a Panna A60 GC with an FID detector using a 30 m packed HP5 column. The conversion rate (R) was calculated according to the equation:  $R = (1 - C_t/C_0) \times 100\%$ , where C<sub>0</sub> and C<sub>t</sub> stand for the initial concentration and after *t* minute reaction concentration of benzaldehyde in a certain amount of methanol.

## **3.2. Acetalization of benzaldehyde with different alcohol:**

Before testing, the catalysts were activated at 150 °C for 6 h. In a typical reaction, 30

mg catalyst was dispersed in 10 mL methanol, ethanol, *n*-propanol, or *n*-butanol in a 20 mL dram vial and immersed in water bath at 25 °C with a magnetic stirrer (800 rpm). The catalyst reaction was initiated by the addition of 3 mmol benzaldehyde. Liquid samples were withdrawn at regular intervals by disposable syringe, and filtered with the 0.22 µm syringe filter, and analyzed by gas chromatography on a Panna A60 GC with an FID detector using a 30 m packed HP5 column. The conversion rate (R) was calculated according to the equation:  $R = (1 - C_t/C_0) \times 100\%$ , where  $C_0$  and  $C_t$  stand for the initial concentration and after  $t$  minute reaction concentration of benzaldehyde in a certain amount of alcohol.

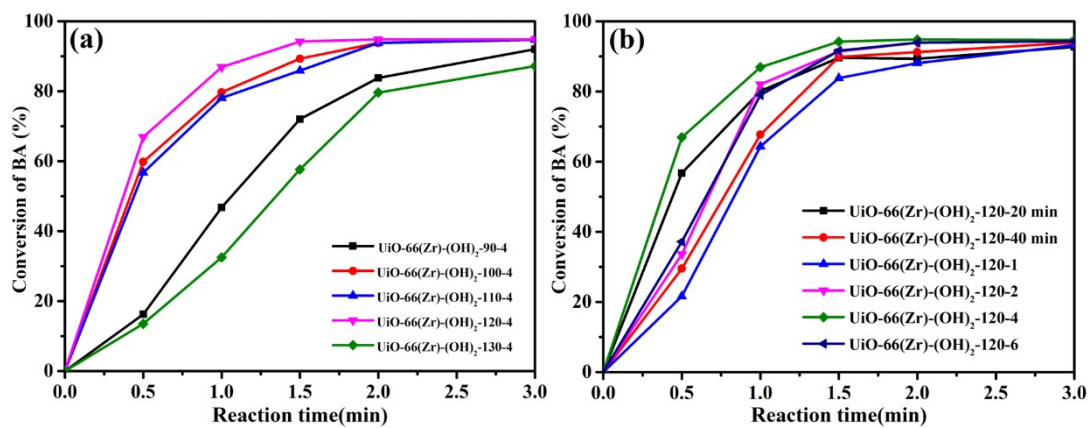
### **3.3. The reusability of catalyst**

The reusability of UiO-66(Zr)-(OH)<sub>2</sub>-green was tested via using 20 mg catalyst in 6 mL methanol with 3 mmol BA at 30 °C. To avoid loss of catalyst, after each cycle the reaction mixture was centrifuged and the settled solution was removed with a dropper, and 6 mL fresh methanol and 3 mmol benzaldehyde were added and used in a new cycle under the same reaction condition.

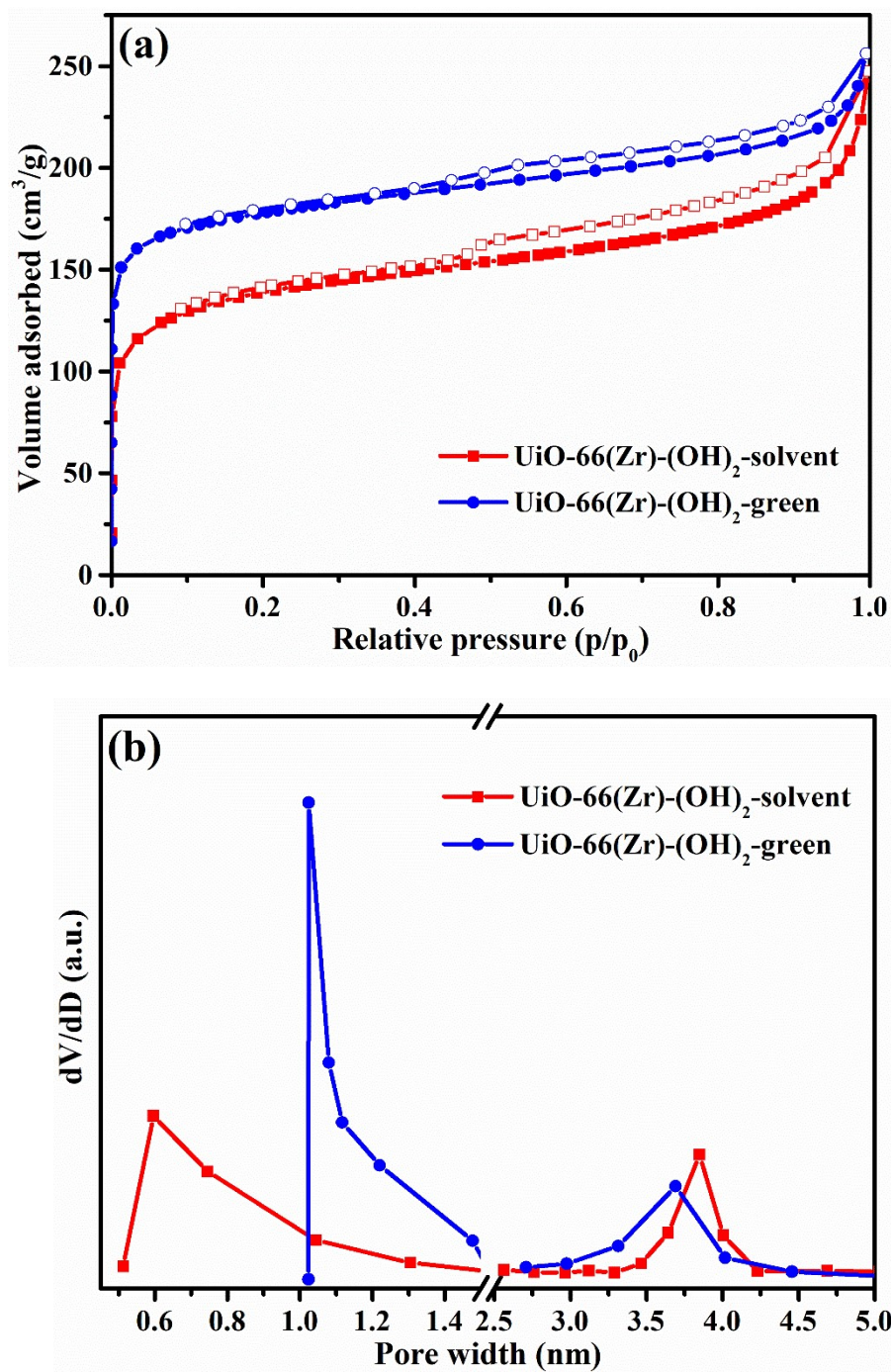
**Table S1** N<sub>2</sub> sorption data and yield of various samples.

| Samples                                  | BET<br>surface<br>area (m <sup>2</sup> /g) | Micropore<br>volume<br>(mL/g) <sup>a</sup> | Mesopore<br>volume<br>(mL/g) <sup>b</sup> | Total pore<br>volume<br>(mL/g) | Yield<br>(%) <sup>c</sup> |
|--|--|--|---|--------------------------------|---------------------------|
| UiO-66(Zr)-(OH) <sub>2</sub> -90-4       | 248  | 0.08                                       | 0.14                                      | 0.20                           | 66.2                      |
| UiO-66(Zr)-(OH) <sub>2</sub> -100-4      | 578  | 0.16                                       | 0.20                                      | 0.36                           | 79.4                      |
| UiO-66(Zr)-(OH) <sub>2</sub> -110-4      | 587  | 0.18                                       | 0.20                                      | 0.37                           | 85.4                      |
| UiO-66(Zr)-(OH) <sub>2</sub> -120-4      | 608  | 0.23                                       | 0.17                                      | 0.39                           | 94.6                      |
| <b>UiO-66(Zr)-(OH)<sub>2</sub>-green</b> |  |  |   |                                |                           |
| UiO-66(Zr)-(OH) <sub>2</sub> -130-4      | 601  | 0.22                                       | 0.18                                      | 0.39                           | 95.1                      |
| UiO-66(Zr)-(OH) <sub>2</sub> -120-20 min | 298  | 0.08                                       | 0.21                                      | 0.26                           | 62.1                      |
| UiO-66(Zr)-(OH) <sub>2</sub> -120-40 min | 444  | 0.14                                       | 0.21                                      | 0.33                           | 76.5                      |
| UiO-66(Zr)-(OH) <sub>2</sub> -120-1      | 531  | 0.18                                       | 0.15                                      | 0.34                           | 78.2                      |
| UiO-66(Zr)-(OH) <sub>2</sub> -120-2      | 578  | 0.21                                       | 0.17                                      | 0.36                           | 83.7                      |
| UiO-66(Zr)-(OH) <sub>2</sub> -120-6      | 567  | 0.22                                       | 0.16                                      | 0.36                           | 95.7                      |
| UiO-66(Zr)-(OH) <sub>2</sub> -solvent    | 482  | 0.16                                       | 0.21                                      | 0.35                           | 69.3                      |

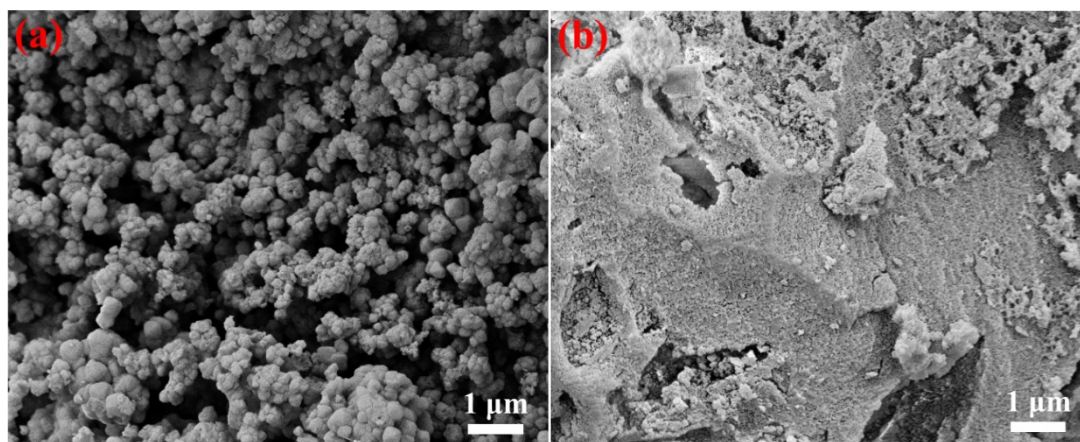
<sup>a</sup> HK method; <sup>b</sup> BJH method; <sup>c</sup> Calculated by the addition amount of BDC-(OH)<sub>2</sub>.



**Fig. S1** The catalytic performance of various samples in the acetalization of benzaldehyde with methanol. Reaction conditions: 6 mmol BA, 15 mL methanol, 20 mg catalyst, 25 °C.

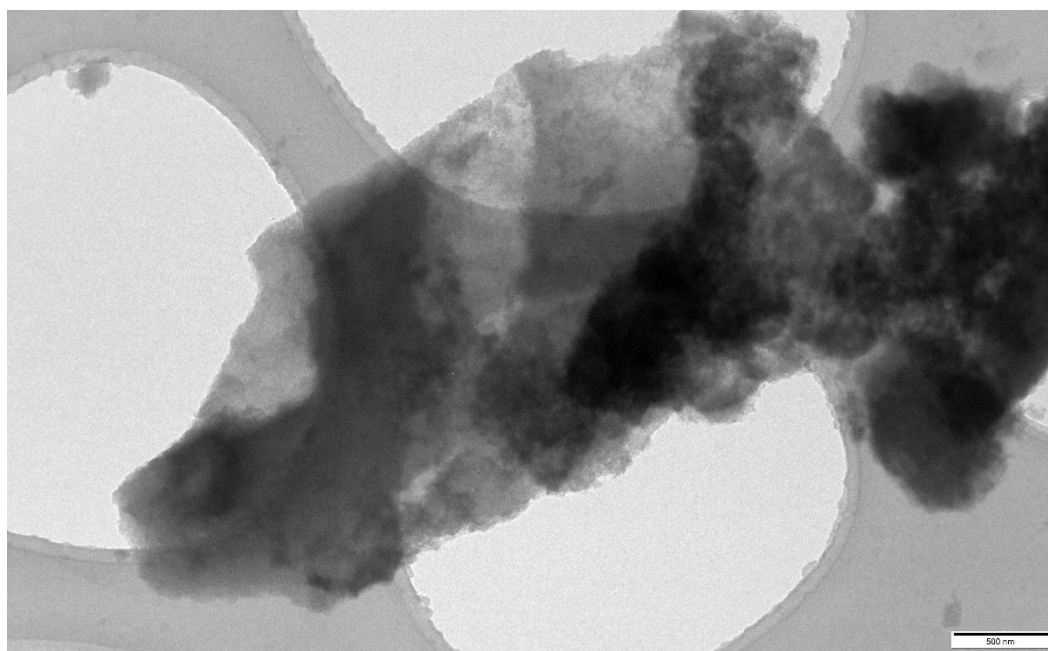


**Fig. S2** (a) N<sub>2</sub> sorption isotherms and (b) the pore size distribution curves of UiO-66(Zr)-(OH)<sub>2</sub>-solvent and UiO-66(Zr)-(OH)<sub>2</sub>-green.

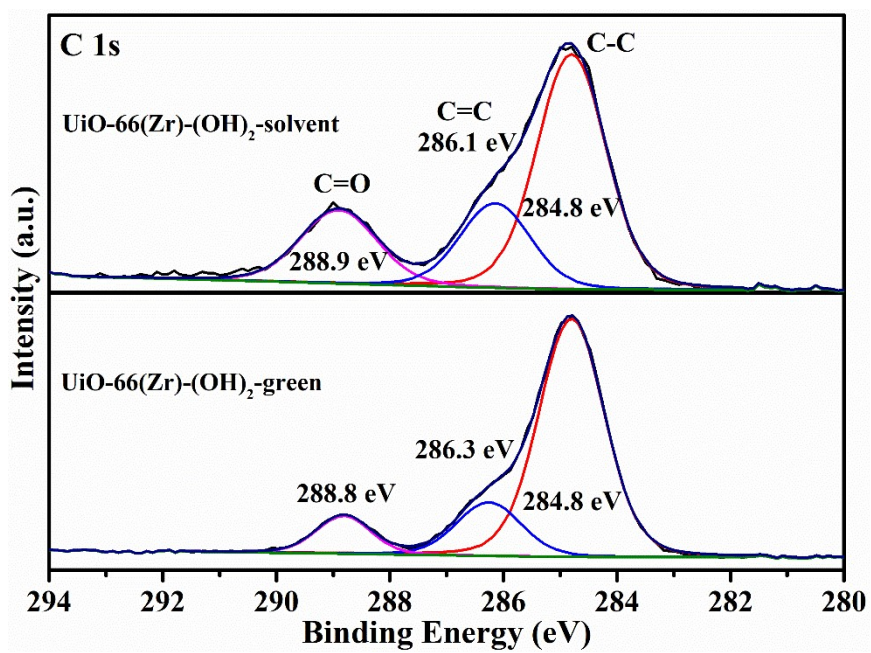


**Fig. S3** SEM images of (a) UiO-66(Zr)-(OH)<sub>2</sub>-solvent and (b) UiO-66(Zr)-(OH)<sub>2</sub>-green.





**Fig. S4** TEM image of UiO-66(Zr)-(OH)<sub>2</sub>-green.

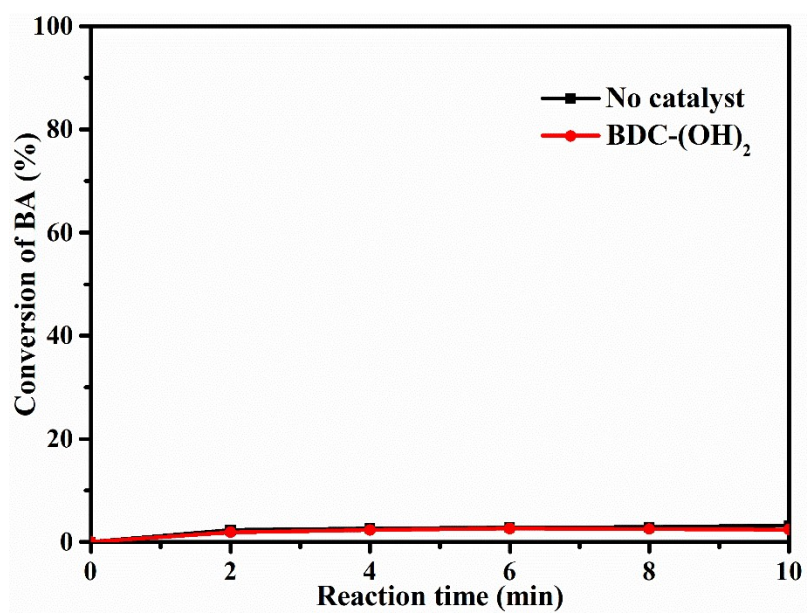


**Fig. S5** The C 1s XPS spectra of UiO-66(Zr)-(OH)<sub>2</sub>-green and UiO-66(Zr)-(OH)<sub>2</sub>-solvent.

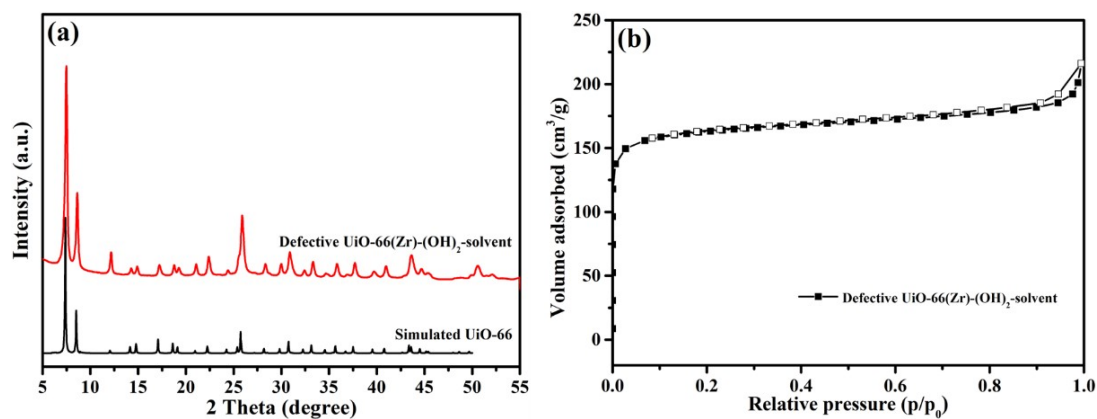
**Table S2** The pH value of various samples.

| Sample | Water | UiO-66(Zr)-(OH) <sub>2</sub> -green | UiO-66(Zr)-(OH) <sub>2</sub> -solvent |
|--------|-------|-------------------------------------|---------------------------------------|
| pH     | 6.80  | 3.03                                | 4.56                                  |

To further explore the acidity of UiO-66(Zr)-(OH)<sub>2</sub>-solvent and UiO-66(Zr)-(OH)<sub>2</sub>-green, 20 mg samples were dispersed in 20 mL water respectively, then the pH of mixtures was measured by pH meter (Table S2). Clearly, the pH of UiO-66(Zr)-(OH)<sub>2</sub>-green (3.03) was lower than UiO-66(Zr)-(OH)<sub>2</sub>-solvent (4.56), indicating that the acidity of UiO-66(Zr)-(OH)<sub>2</sub>-green is stronger than UiO-66(Zr)-(OH)<sub>2</sub>-solvent. The result could be ascribed that UiO-66(Zr)-(OH)<sub>2</sub>-green possess more defects than UiO-66(Zr)-(OH)<sub>2</sub>-solvent, and the density of defects can manipulate the acidity of UiO-66(Zr)-(OH)<sub>2</sub>.

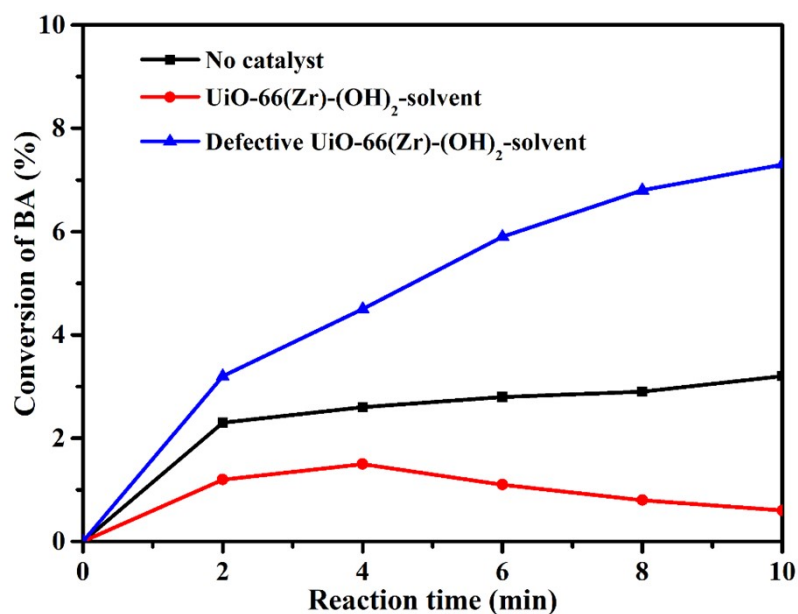


**Fig. S6** The catalytic performance of BDC-(OH)<sub>2</sub> in acetalization of benzaldehyde with methanol. Reaction conditions: 6 mmol BA, 15 mL methanol, 20 mg catalyst, 25 °C.



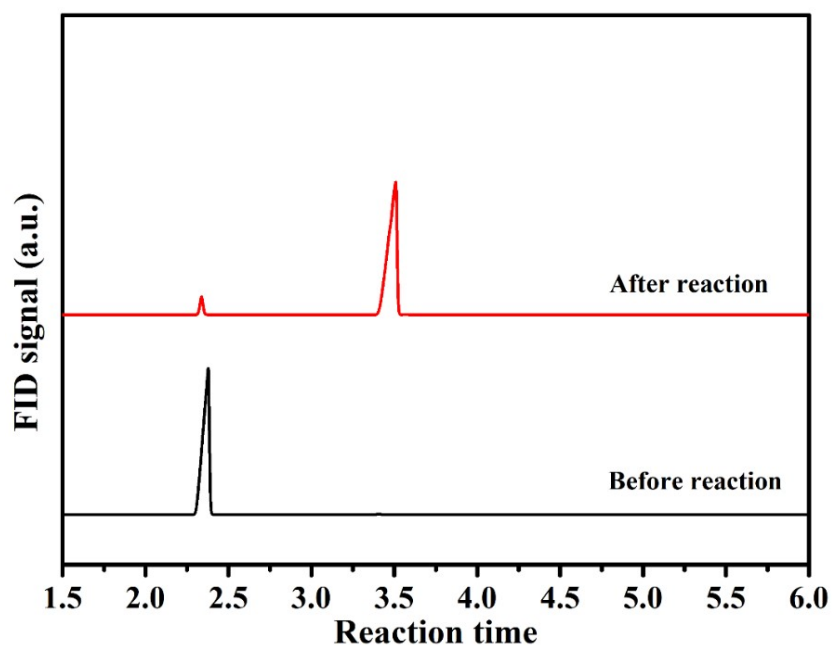
**Fig. S7** (a) XRD pattern, (b) N<sub>2</sub> sorption isotherm of defective UiO-66(Zr)-(OH)<sub>2</sub>-solvent.

The powder XRD pattern of defective UiO-66(Zr)-(OH)<sub>2</sub>-solvent was almost same as that of simulated UiO-66, confirming that the UiO-66 structure was retained (Fig. S6a). The N<sub>2</sub> adsorption isotherm of defective UiO-66(Zr)-(OH)<sub>2</sub>-solvent exhibited type I isotherm, indicating that defective UiO-66(Zr)-(OH)<sub>2</sub>-solvent is a microporous material (Fig. S6b). The BET surface area of defective UiO-66(Zr)-(OH)<sub>2</sub>-solvent reached 603 m<sup>2</sup>/g.



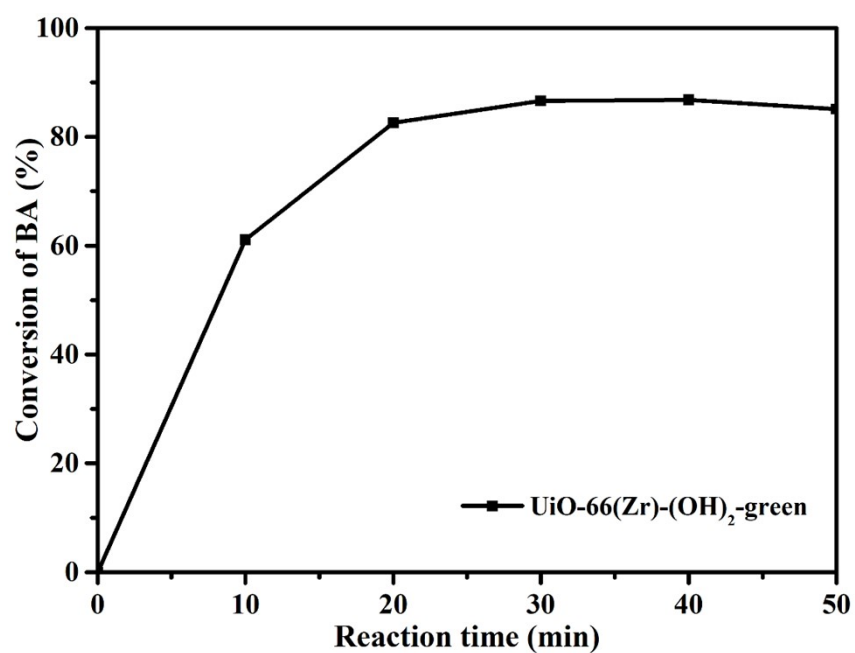
**Fig. S8** The catalytic performance of various samples in the acetalization of benzaldehyde with methanol. Reaction conditions: 6 mmol BA, 15 mL methanol, 20 mg catalyst, 25 °C.

The catalytic performance of defective UiO-66(Zr)-(OH)<sub>2</sub>-solvent was better than UiO-66(Zr)-(OH)<sub>2</sub>-solvent (Fig. S8). The result indicated that the defect density in UiO-66(Zr)-(OH)<sub>2</sub> plays a crucial role for manipulating catalytic activity. The hierarchical pore not only could make the defect sites more accessibility but also benefitted for mass transport that can accelerate reaction process.



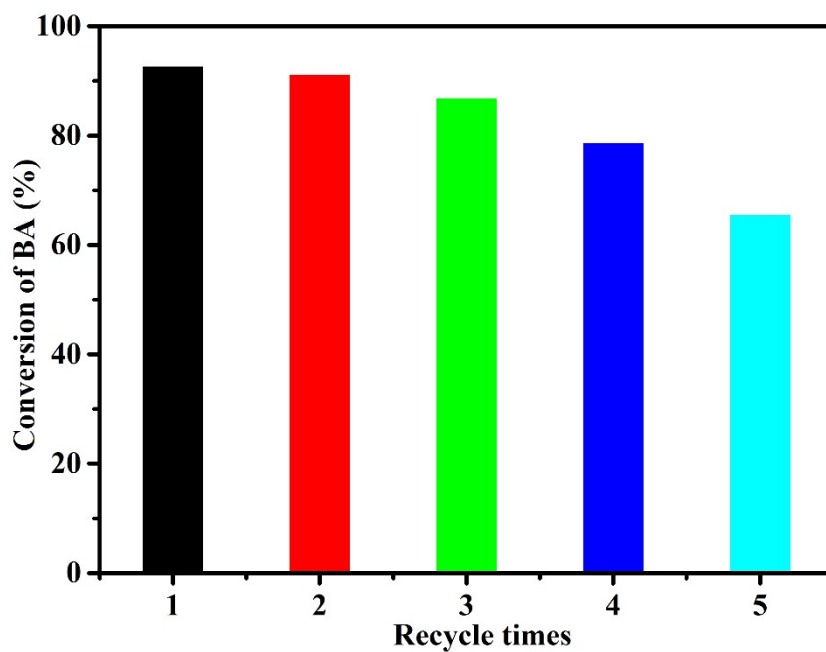
**Fig. S9** GC-FID chromatograms of before and after reaction solutions.

The solution after reaction was filtered with the 0.22  $\mu\text{m}$  syringe filter and tested by GC. Clearly, only (dimethoxymethyl)benzene and small amount of benzaldehyde could be detected (Fig. S9), confirming that there is no by-product in this reaction.



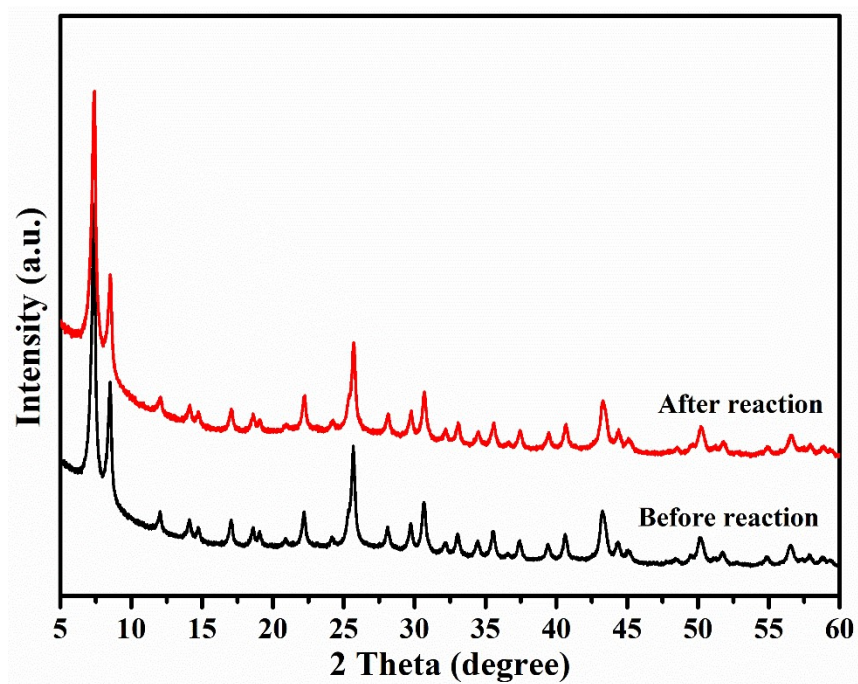
**Fig. S10** The catalytic performance of UiO-66(Zr)-(OH)<sub>2</sub>-green in the acetalization of benzaldehyde with methanol. Reaction condition: 5 mL BA, 50 mL methanol, 10 mg catalyst, 30 °C.



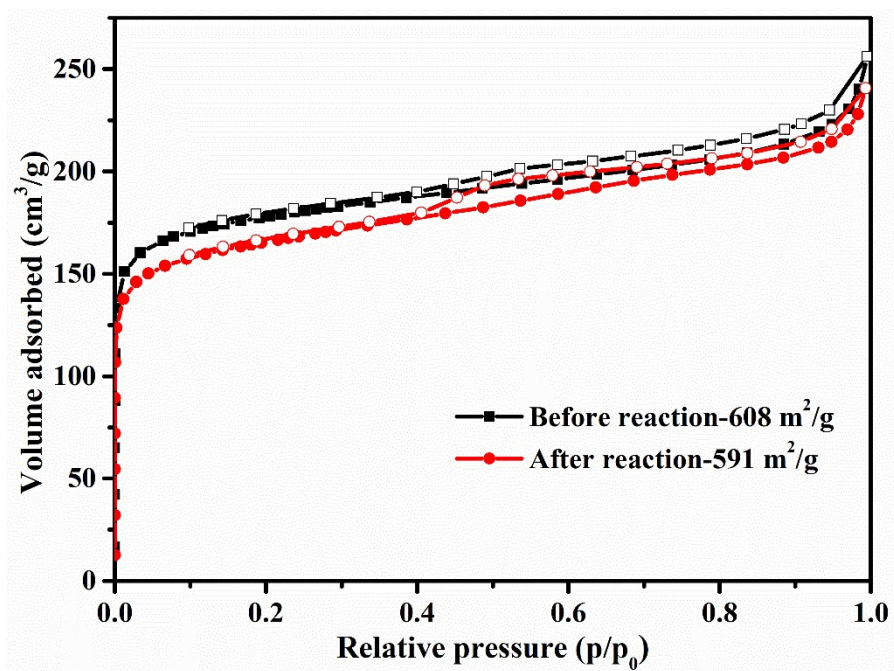


**Fig. S11** The reusability of UiO-66(Zr)-(OH)<sub>2</sub>-green in acetalization reaction. Reaction conditions: 3 mmol BA, 9 mL methanol, 10 mg catalyst, 25 °C, 4 min.

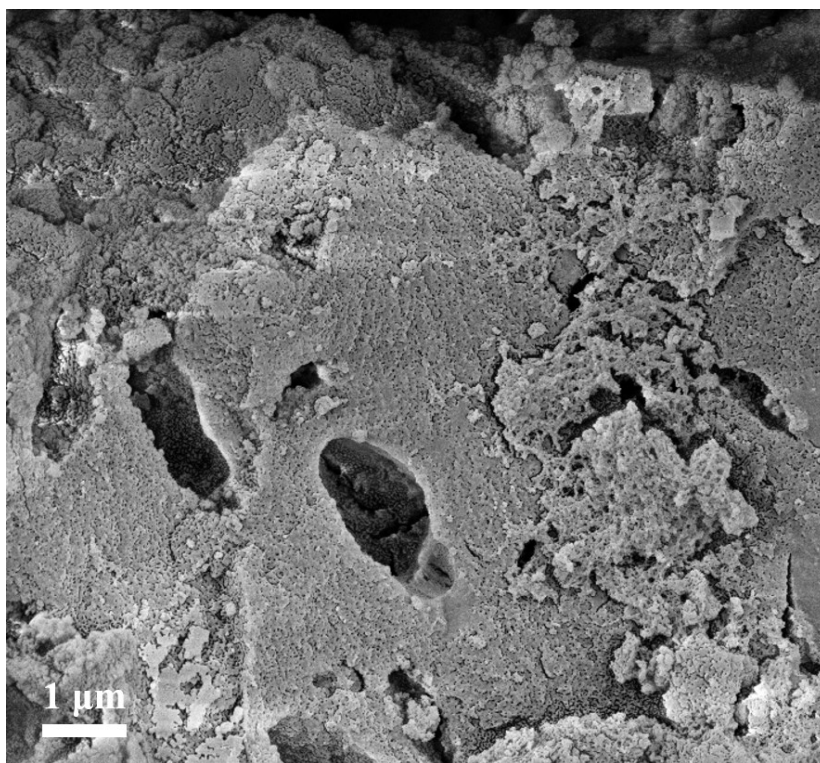
The reusability of UiO-66(Zr)-(OH)<sub>2</sub>-green was evaluated by acetalization of benzaldehyde with methanol when the catalyst dosage was reduced to 10 mg. However, after 2nd cycle, the catalytic activity was decreased and only 65.4% benzaldehyde could be converted after 5th cycle at a reaction time of 4 min (Fig. S11).



**Fig. S12** XRD patterns of UiO-66(Zr)-(OH)<sub>2</sub>-green before and after reaction.



**Fig. S13** N<sub>2</sub> sorption isotherms of UiO-66(Zr)-(OH)<sub>2</sub>-green before and after reaction.



**Fig. S14** SEM image of UiO-66(Zr)-(OH)<sub>2</sub>-green after reaction.

**Table S3** Comparison of catalytic activities over several MOFs and MOFs based catalysts in acetalization reaction of benzaldehyde with methanol.

| Catalyst  | Active species and content (wt %) | Dosage of catalyst (mg) | BA dosage (mmol) | Temp. (°C) | Time (min) | Conversion rate (wt %) | TOF (h <sup>-1</sup> ) <sup>a</sup> | Activity (mmol·g <sup>-1</sup> ·h <sup>-1</sup> ) <sup>b</sup> | Ref.             |
|---|-----------------------------------|-------------------------|------------------|------------|------------|------------------------|-------------------------------------|--|------------------|
| MIL-100(Fe)                                       | Fe(~23)                           | 10                      | 49               | 30         | 60         | 87.0                   | 1035                                | 4263   | 1                |
| MIL-100(Fe)-S                                     | Fe(~23)                           | 20                      | 2.94             | RT         | 15         | 86.0                   | 25                                  | 506  | 2                |
| MIL-101/PTA                                       | PTA + Cr(-)                       | 10                      | 3.34             | 25         | 1440       | ~95.0                  | 1320                                | 13   | 3                |
| MIL-101Cr-NO <sub>2</sub>                         | Cr(-)                             | 10                      | 3.34             | RT         | 90         | 99.0                   | 76                                  | 220  | 4                |
| MIL-100(Fe)                                       | Fe(21)                            | 10                      | 2.94             | 40         | 1260       | 84.0                   | 3                                   | 12   | 5                |
| Fe(BTC)   | Fe(25)                            | 9                       | 2.94             | 40         | 1260       | 84.0                   | 3                                   | 13   | 5                |
| UiO-66-NO <sub>2</sub>                            | Zr(~28.3)                         | 50                      | 0.94             | 30         | 180        | ~100                   | 2                                   | 6  | 6                |
| UiO-66(Zr)-NO <sub>2</sub> -Green                 | Zr(~)                             | 35                      | 3                | RT         | 30         | 93.0                   | 50                                  | 159  | 7                |
| MIL-101(Cr)-NO <sub>2</sub>                       | Cr(~14)                           | ~44                     | 1                | 30         | ~390       | ~90.0                  | 3                                   | 3  | 8                |
| Cu <sub>3</sub> (BTC) <sub>2</sub>                | Cu(23.2)                          | 50                      | 0.94             | RT         | 1440       | 88.0                   | <1                                  | <1   | 9                |
| CoFe <sub>2</sub> O <sub>4</sub> @Polmer @MIL-100 | --                                | 10                      | 2                | 40         | 10         | 97.7                   | 921                                 | 1172   | 10               |
| UiO-66(Zr)  | Zr(32.9)                          | 50                      | 0.98             | 28         | 60         | 91.0                   | 5                                   | 18   | 11               |
| BNNs/MOF-2  | --                                | 60                      | 0.98             | RT         | 720        | 70.4                   | --                                  | <1   | 12               |
| UiO-66(Zr)-(OH) <sub>2</sub> -green               | Zr(32.8) <sup>a</sup>             | 20                      | 6                | 25         | 2          | 95.2                   | 2380                                | 8568   | <b>This work</b> |

<sup>a</sup> TOF = (mole number of converted BA) / (mole of active species content in catalyst × reaction time (h)). <sup>b</sup> Activity = millimole number of converted BA per gram catalyst per hour.

## References

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