

## Supporting Information

### **Closed-Loop Recycling: Upcycling PET into MOFs for Catalytic Hydrogenolysis and High-Purity Monomer Recovery**

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## S.1 Experimental Section

### S.1.1. Materials

All the chemicals were of analytical grade and used in the experiments without further purification. *N,N*-dimethylformamide (DMF), ethanol (CH<sub>3</sub>CH<sub>2</sub>OH) and methanol (CH<sub>3</sub>OH) were purchased from Sinopharm Pharmaceutical Co. Polyethylene glycol terephthalate (PET) and polybutylene terephthalate (PBT) were purchased from Dongguan Zhangwood Hongxin plastic raw materials management department. PET bottles were obtained from the PET package of "Nongfu mountain spring mineral water". Formic acid (HCOOH), 1,2-ethylene glycol dibenzoate (EDB), deuterium chloroform (CDCl<sub>3</sub>), dimethyl sulfoxide (DMSO-d<sub>6</sub>), zirconium tetrachloride (IV) (ZrCl<sub>4</sub>), caesium carbonate (Cs<sub>2</sub>CO<sub>3</sub>), hafnium chloride (HfCl<sub>4</sub>), diammonium cerium (IV) nitrate ((NH<sub>4</sub>)<sub>2</sub>Ce(NO<sub>3</sub>)<sub>6</sub>), titanium tetrakisopropanolate (C<sub>12</sub>H<sub>28</sub>O<sub>4</sub>Ti), cobaltous nitrate hexahydrate (Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O), strontium chloride hexahydrate (SrCl<sub>2</sub>·6H<sub>2</sub>O), manganese chloride tetrahydrate (MnCl<sub>2</sub>·4H<sub>2</sub>O), cadmium chloride hemi (penta)hydrate (CdCl<sub>2</sub>·2.5H<sub>2</sub>O), nickel acetate (NiC<sub>4</sub>H<sub>6</sub>O<sub>4</sub>·4H<sub>2</sub>O), ferric chloride hexahydrate (FeCl<sub>3</sub>·6H<sub>2</sub>O), cupric chloride (CuCl<sub>2</sub>), aluminum nitrate nonahydrate (Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O), vanadium (III) chloride (VCl<sub>3</sub>), magnesium sulfate (MgSO<sub>4</sub>), chromium (III) nitrate nonahydrate (CrH<sub>18</sub>N<sub>3</sub>O<sub>18</sub>), zinc acetate dihydrate (C<sub>4</sub>H<sub>8</sub>O<sub>4</sub>Zn·2H<sub>2</sub>O), terbium nitrate hexahydrate (H<sub>12</sub>N<sub>3</sub>O<sub>15</sub>Tb), were purchased from Anhui Zesheng Technology company. Yttrium hexahydrate trinitrate (YN<sub>3</sub>O<sub>9</sub>·6H<sub>2</sub>O) and Erbium (III) Nitrate Pentahydrate (ErN<sub>3</sub>O<sub>9</sub>·5H<sub>2</sub>O), were purchased from Meryer (Shanghai) Chemical Technology Co.

### S.1.2. PET-derived *hcp* UiO-66 and continuous synthesis

105 mg of ZrCl<sub>4</sub> and 75 mg of PET powder were dissolved in 3 mL of formic acid, mixed evenly and put into a 20 mL polytetrafluoroethylene lined reactor and heated at 160 °C for 36 hours. After the reaction, the reactor was cooled to room temperature and 1 mL formic acid filtrate was collected for the next reaction. The solid white precipitate was washed several times with DMF and methanol dried overnight in an oven at 60 °C and activated under a dynamic vacuum of 120 °C. Subsequent synthesis is similar to this procedure.

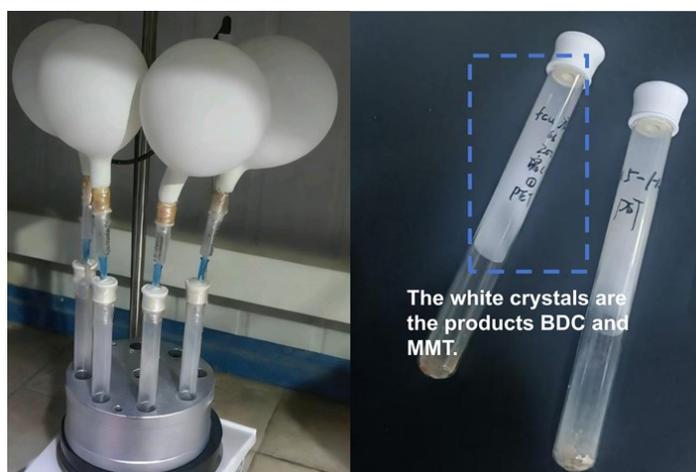
Continuous synthesis of *hcp* UiO-66 (in a cyclic process) employs the same conditions, but the solvent is replenished from the previous filtration, with additional fresh metal salt, PET, and formic acid to compensate for volatilities and losses.

### S.1.3. EDB hydrogenolysis

1,2-ethanediol dibenzoate (EDB) (30.0 mg, 0.11 mmol) and 5 mol% *hcp* UiO-66 powder were added to a (15×150) mm glass test tube. The air inside is replaced three times with H<sub>2</sub>, and then a hydrogen balloon is inserted into the glass tube and heated at 220 °C for one day. After the reaction, the tube was cooled to room temperature, 9.9 mg mesitylene (internal standard) and 1 mL CDCl<sub>3</sub> were added, and <sup>1</sup>H NMR characterization of the product was performed.

### S.1.4. PET hydrogenolysis

PET powder (21.3 mg, 0.11 mmol.) and *hcp* UiO-66 powder (13.2 mg, 0.0055 mmol.) were added together into a (15×150) mm glass test tube, the hydrogen balloon was inserted into the test tube and the test tube was heated at 260 °C without stirring, the system was maintained at ambient pressure (approximately 1 atm). During the reaction, terephthalic acid sublimed and crystallized at the top of the tube, while the unreacted PET and catalyst remained at the bottom of the tube (the white crystalline material observed at the upper, cooler region of the reaction tube is the sublimed and purified BDC and MMT product). After the reaction was completed and cooled down, 1 mL DMSO-d<sub>6</sub> and 13 mg of mesitylene (internal standard) were added to the test tube. 1 mL of the reaction mixture



was used for nuclear magnetic analysis. PBT hydrolysis uses the same process as above, only replacing PET with PBT (28.18 mg, 0.11 mmol).

### S.1.5. Cyclic experiment

During the degradation reaction, the white solid product BDC and MMT sublimed on the top of the test tube, while the catalyst was coated with unreacted PET at the bottom of the test tube. After the first run for 8 days, the white solid product at the top of the test tube was scraped out and dissolved in DMSO-d<sub>6</sub> for nuclear magnetic analysis. At the same time, the same amount of fresh PET was added to the test tube for the second catalytic run.

### S.1.6. Quantify the yields of PET and PBT hydrogenolysis

The yield was quantified by <sup>1</sup>H NMR spectroscopy using an internal standard method. Upon completion of the reaction, the mixture was dissolved in 1 mL of DMSO-d<sub>6</sub>, and a precisely weighed amount of mesitylene (mass denoted as  $m_{IS}$ , approximately 13 mg) was added as the internal standard.

In the <sup>1</sup>H NMR spectrum, the aromatic proton signal of mesitylene appears at  $\delta \approx 6.76$  ppm, while the aromatic proton signals of terephthalic acid (BDC) and monomethyl terephthalate (MMT) are observed at  $\delta \approx 8.05$  ppm and  $\delta \approx 8.06$  ppm, respectively. Based on the number of protons corresponding to these characteristic peaks (3 for mesitylene, 4 for both BDC and MMT), the yield was calculated from the integrated peak areas.

First, the molar amount of the internal standard (IS) was determined from its mass:

$$n_{IS} = \frac{m_{IS}}{M_{IS}},$$

where  $M_{IS}=120.19 \text{ g}\cdot\text{mol}^{-1}$  is the molar mass of mesitylene.

Subsequently, the molar amount of the product (BDC or MMT),  $n_{\text{prod}}$ , was calculated by comparing the integrated areas and the corresponding proton numbers:

$$n_{prod} = \frac{A_{prod} \times N_{IS} \times n_{IS}}{A_{IS} \times N_{prod}} = \frac{A_{prod} \times 3 \times n_{IS}}{A_{IS} \times 4}$$

Here,  $A_{prod}$  and  $A_{IS}$  are the integrated areas of the characteristic peaks for the product and the internal standard, respectively;  $N_{IS} = 3$  and  $N_{prod} = 4$  are the corresponding numbers of protons.

To simplify the quantification process, the integrated peak area for the internal standard (mesitylene) was normalized to a reference value of 3. The integrated peak area for each product ( $A_{prod}$ ) is thus reported relative to this normalized value. Consequently, the molar amount of the product ( $n_{prod}$ ) can be conveniently calculated using the formula:

$$n_{prod} = \frac{A_{prod} \times n_{IS}}{4},$$

where  $n_{IS}$  is the molar amount of the internal standard.

Finally, the percentage yield was obtained by comparing the actual molar amount of the product with the theoretical maximum molar amount derivable from complete PET hydrolysis ( $n_{PET} = 0.11$  mmol):

$$Yield = \frac{n_{prod}}{n_{PET}} \times 100\%$$

The selectivity for any given product (BDC and MMT) was calculated using the following formula:

$$selectivity = \frac{n_{prod}}{n_{BDC} + n_{MMT}} \times 100\%$$

For PBT, the amount of additive used is 0.11 mmol, identical to that for PET, and the yield is calculated in the same manner as for PET.

## **S.2. Characterization**

The synthesized MOF materials were characterized following the standard characterization techniques. Structural analysis of the prepared materials was performed at  $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$  using a Smart Lab 9 kW high power X-ray diffractometer equipped with a Cu target radiation. The TGA images were obtained using a Perkinelmer Synchronous Thermal Analyzer (STA) 6000 unit heated in an air stream at a rate of  $5\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ . The surface area of the sample was measured using the Brunauer-Emmett-Teller (BET) method on a Micromeritics 3Flex instrument. FT-IR images were obtained using the Thermo Scientific Nicolet 6700 instrument. The surface element analysis of MOF samples was determined by Thermo Fisher Scientific K-Alpha X-ray photoelectron spectrometer. The morphology of MOF samples was analyzed by JEOL JSM-7900F ultra-high resolution field emission scanning electron microscopy.  $^1\text{H}$  NMR tests of the reaction products were performed on the Bruker AVANCE NEO 400 M instrument.

### S.3. Characterization of materials

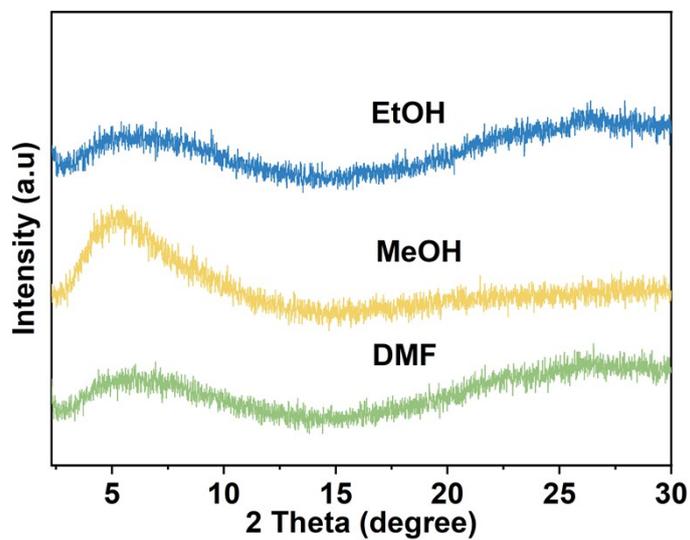


Figure S1. The PXRD patterns of UiO-66 synthesized in different solvents.

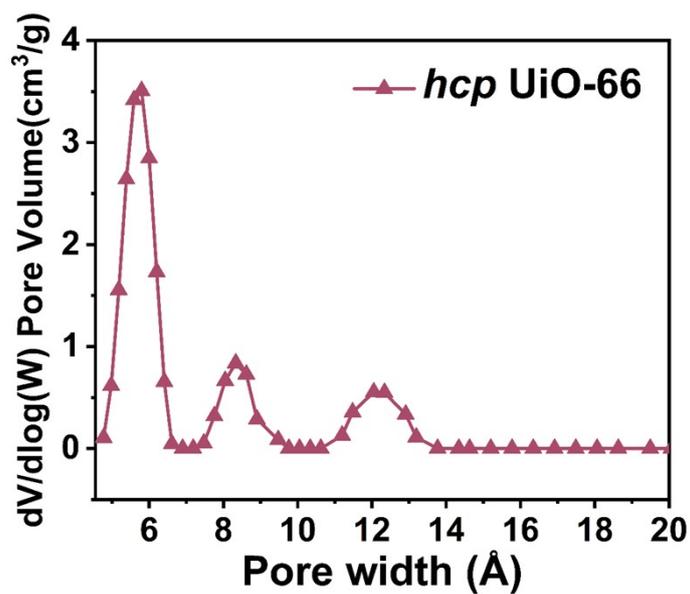
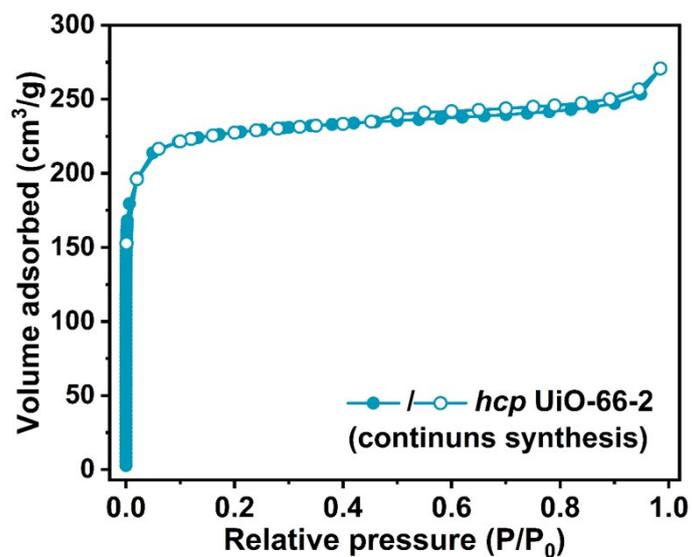
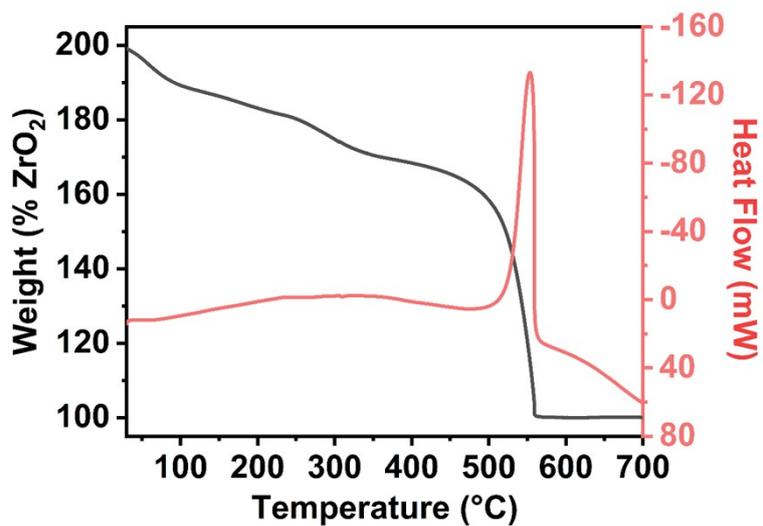


Figure S2. Pore size distributions of PET-derived *hcp* UiO-66.



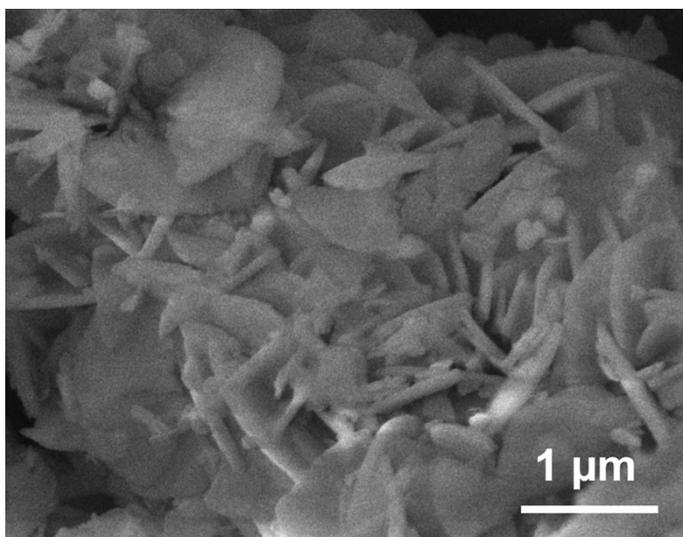
**Figure S3.** N<sub>2</sub> adsorption–desorption isotherms of PET-derived UiO-66 synthesized via continuous synthesis.



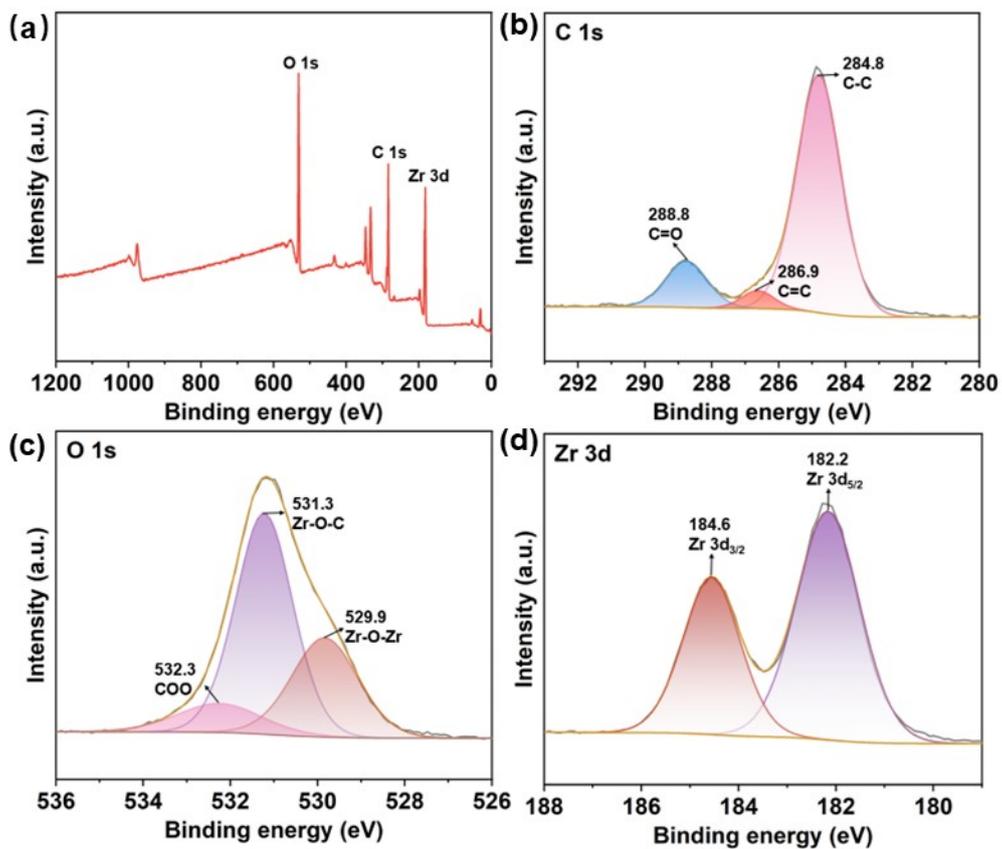
**Figure S4.** TGA -DSC curves of PET-derived UiO-66

**Table S1.** Yield of synthetic MOFs.

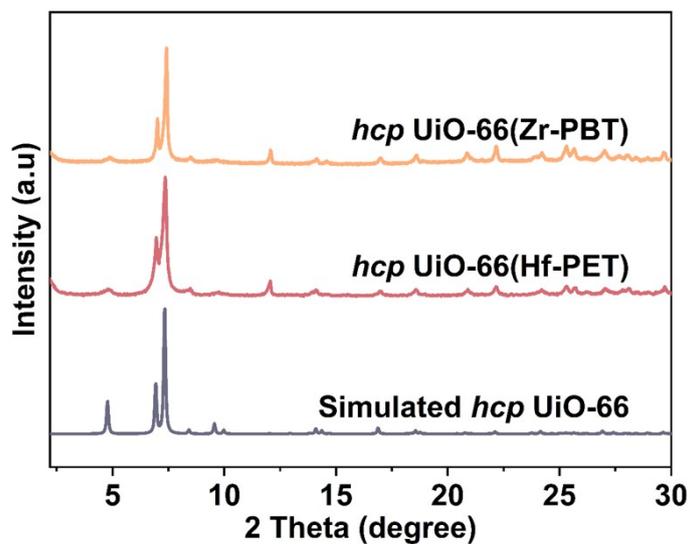
Sample	MOF yield based on Zr (%)
<i>hcp</i> UiO-66	9.0
<i>hcp</i> UiO-66-1	8.3
<i>hcp</i> UiO-66-2	8.7
<i>hcp</i> UiO-66-3	9.0



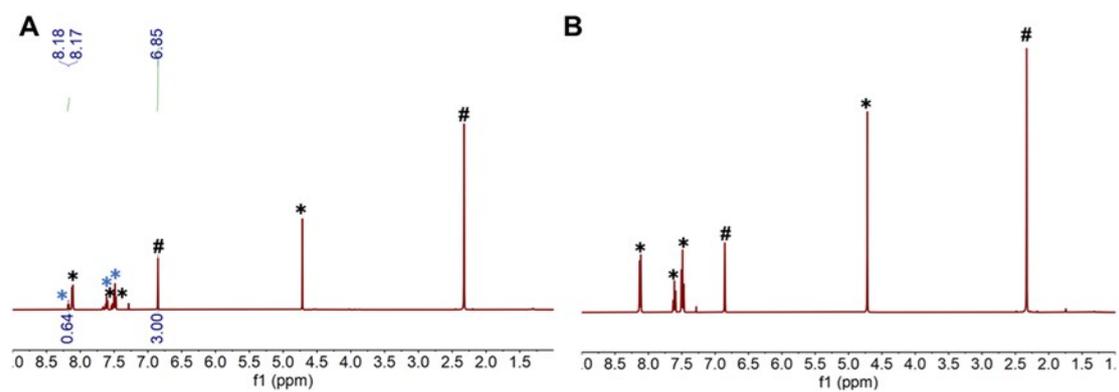
**Figure S5.** SEM image of *hcp* UiO-66-2 synthesized using the recycling solvent.



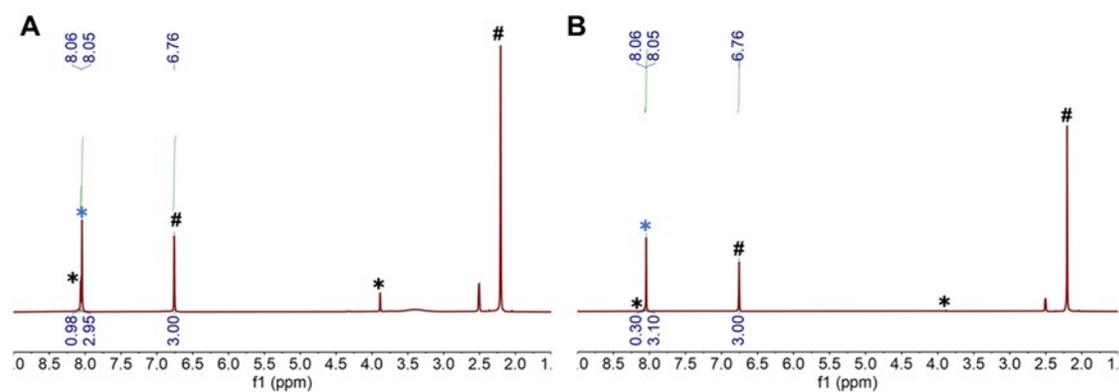
**Figure S6.** (a) XPS survey spectra, (b) C 1s spectra, (c) O 1s spectra, and (d) Zr 3d spectra of PET-derived *hcp* UiO-66.



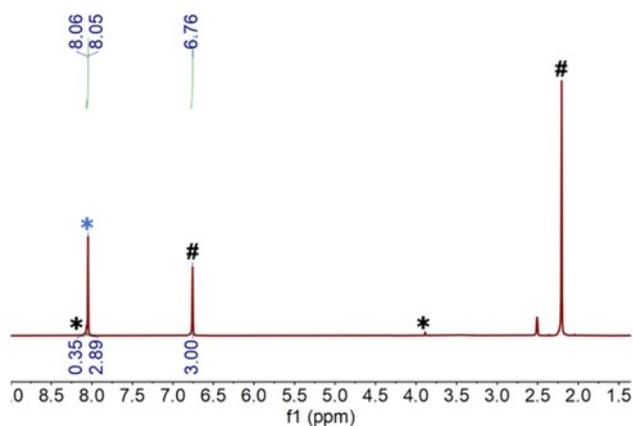
**Figure S7.** *hcp* UiO-66 samples were synthesized with PBT as linker sources and Hf salts.



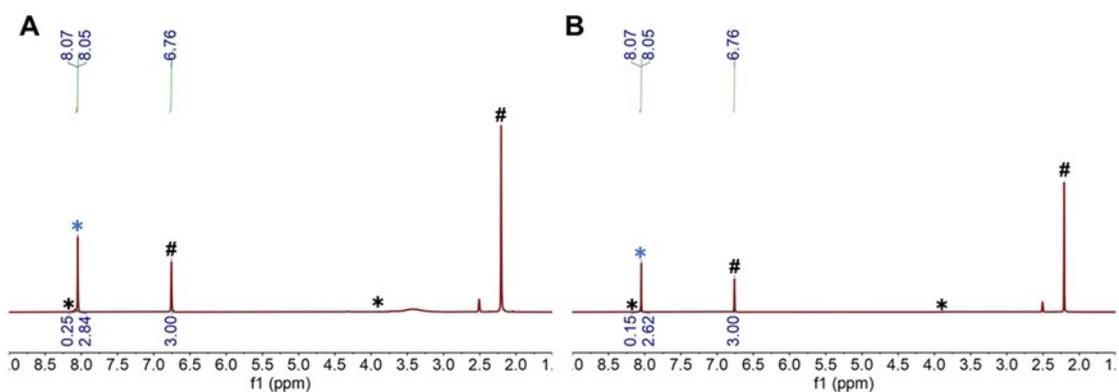
**Figure S8.** <sup>1</sup>H NMR spectra of the EDB catalyzed by *hcp* UiO-66 (A) and no catalyst (B) under H<sub>2</sub>. The benzoic acid signal is represented by a blue asterisk (\*), the EDB signal is represented by a black asterisk (\*), and the internal standard methylene toluene signal is represented by a (#) symbol.



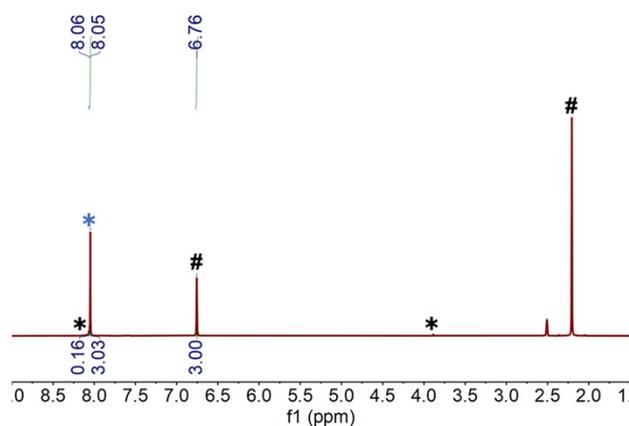
**Figure S9.** <sup>1</sup>H NMR spectra of the commercial PET particle catalyzed by *hcp* UiO-66 under H<sub>2</sub> (A) and N<sub>2</sub> (B). The BDC signal is represented by a blue asterisk (\*), the by-product MMT signal is represented by a black asterisk (\*), and the internal standard methylene toluene signal is represented by a (#) symbol.



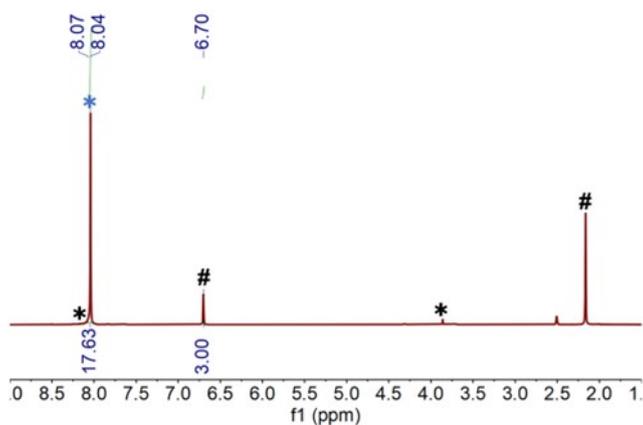
**Figure S10.**  $^1\text{H}$  NMR spectra of the PET bottles catalyzed by *hcp* UiO-66 under  $\text{H}_2$ . The BDC signal is represented by a blue asterisk (\*), the by-product MMT signal is represented by a black asterisk (\*), and the internal standard methylene toluene signal is represented by a (#) symbol.



**Figure S11.**  $^1\text{H}$  NMR spectra of the commercial PET without catalyst under  $\text{H}_2$  (A) and  $\text{N}_2$  (B). The BDC signal is represented by a blue asterisk (\*), the by-product MMT signal is represented by a black asterisk (\*), and the internal standard methylene toluene signal is represented by a (#) symbol.



**Figure S12.**  $^1\text{H}$  NMR spectra of the commercial PBT particle catalyzed by *hcp* UiO-66. The BDC signal is represented by a blue asterisk (\*), the by-product MMT signal is represented by a black asterisk (\*), and the internal standard methylene toluene signal is represented by a (#) symbol.

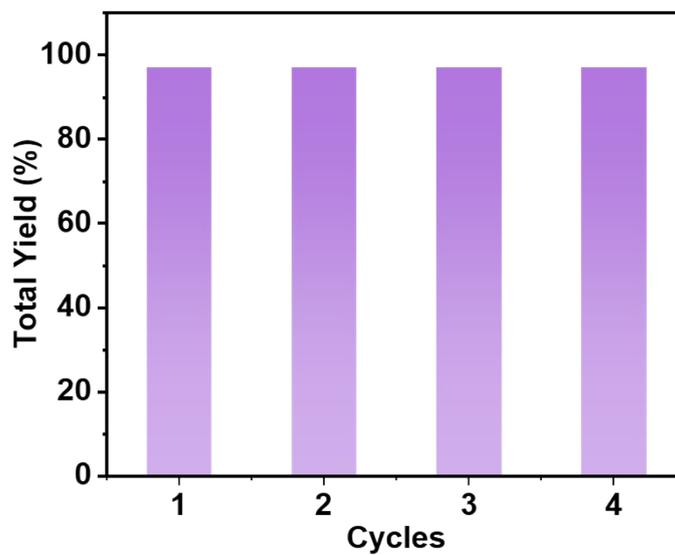


**Figure S13.**  $^1\text{H}$  NMR spectra of the commercial PET particle continuously catalyzed by *hcp* UiO-66 under  $\text{H}_2$ . The BDC signal is represented by a blue asterisk (\*), the by-product MMT signal is represented by a black asterisk (\*), and the internal standard methylene toluene signal is represented by a (#) symbol.

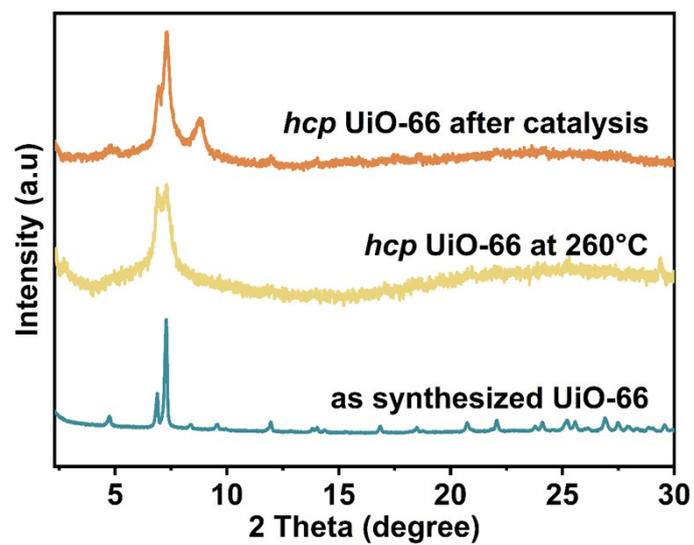
**Table S2.** The reported activity of catalytic hydrolyzed PET.

Entry	Polyester	Catalysts	Atmosphere	t[h]	T[°C]	Yield of TA <sup>b</sup> [%]
1	PET <sup>[a]</sup>	C/MoO <sub>2</sub>	H <sub>2</sub>	24	260	87
2	PET <sup>[a]</sup>	MoCo@NC	H <sub>2</sub>	10	260	91
3	PBT <sup>[a]</sup>	MoCo@NC	H <sub>2</sub>	20	260	90
4	PET <sup>[a]</sup>	Hf(OTf) <sub>4</sub> + Pd/C	H <sub>2</sub>	24	265	98
5	PET <sup>[b]</sup>	<i>hcp</i> UiO-66(Zr)	H <sub>2</sub>	24	260	73

[a] Commercial PET, [b] PET bottles.



**Figure S14.** The total yield corresponding to each cycle when using *hcp* UiO-66 as a catalyst at 260 °C



**Figure S15.** PXRD patterns of *hcp* UiO-66 after four cycles of catalysis (orange) and heating UiO-66 at 260 °C (yellow).