

# Supporting Information

Hierarchical large-pore MOFs templated from poly(ethylene oxide)-*b*-  
polystyrene diblock copolymer with tuneable pore sizes

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## S1. Experiment section

### S1.1 Chemicals and materials

PEO<sub>117</sub>-*b*-PS<sub>50</sub> and PEO<sub>117</sub>-*b*-PS<sub>150</sub> were supplied by Hangzhou Xinqiao Biotechnology Co., Ltd. Cerium (IV) ammonium nitrate ((NH<sub>4</sub>)<sub>2</sub>Ce(NO<sub>3</sub>)<sub>6</sub>) was purchased from Shanghai Macklin Biochemical Co., Ltd. Sodium perchlorate monohydrate (NaClO<sub>4</sub>·H<sub>2</sub>O) was purchased from Sinpharm Chemical Reagent Co., Ltd. 1,4-benzenedicarboxylic acid (BDC) were supplied by Aladdin Chemistry Co., Ltd. (Shanghai, China). 1,3,5-Trimethylbenzene (TMB) was supplied by Shanghai Aladdin Bio-Chem Technology Co., LTD. Tetrahydrofuran (THF), N,N-dimethylformamide (DMF) and acetic acid (AA) were purchased from Shanghai Titan Scientific Co., Ltd. All reagents were of analytical grade and used without further purification. The applied water (18.1 MΩ·cm<sup>-1</sup>) in the experiments was purified from a NW Ultrapure Water System (Heal Force, China).

### S1.2 Synthesis of HP-UiO-Ce

Under typical optimized synthesis, 18 mg PEO<sub>117</sub>-*b*-PS<sub>50</sub> or PEO<sub>117</sub>-*b*-PS<sub>150</sub> diblock copolymers was completely dissolved in 200 μL THF. Then, 800 μL water was added under magnetic stirring. After stirring for a while, 40 μL AA (0.68 mmol, 1.7 equiv.) and 40 mg NaClO<sub>4</sub> (0.28 mmol, 0.7 equiv.) were added. As a control, some samples were also synthesized without the addition of NaClO<sub>4</sub>. The mixture was stirred to form a homogeneous solution. Subsequently, 218 mg (NH<sub>4</sub>)<sub>2</sub>Ce(NO<sub>3</sub>)<sub>6</sub> (0.4 mmol, 1 equiv.) and 66 mg BDC (0.4 mmol, 1 equiv.) were added into above mixture. The mixture was stirred for 15 min at 60 °C. The resultant solid was isolated by centrifugation and washed with water once and DMF twice. To remove the template, the as-synthesized sample was soaked in DMF for one day and ethanol for two days at 60 °C, during which time ethanol was changed every day. Finally, the product

was dried overnight at 60 °C under vacuum.

### **S1.3 Synthesis of HP-UiO-Ce with TMB**

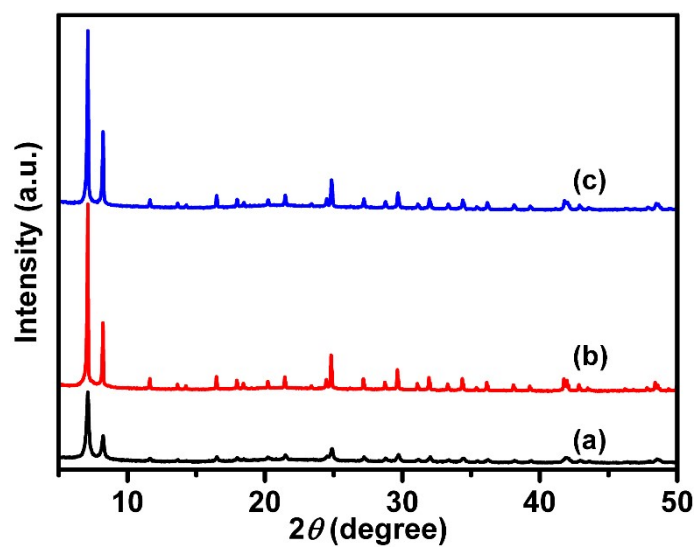
18 mg PEO<sub>117</sub>-*b*-PS<sub>50</sub> and different amounts of TMB (2, 5 and 6 μL, weight ratio of 0.10-0.29 to diblock copolymers) were completely dissolved in 200 μL THF. Then, 800 μL water was added under magnetic stirring. After stirring for a while, 40 μL AA (0.68 mmol, 1.7 equiv.) and 40 mg NaClO<sub>4</sub> (0.28 mmol, 0.7 equiv.) were added. The mixture was stirred to form a homogeneous solution. Subsequently, 218 mg (NH<sub>4</sub>)<sub>2</sub>Ce(NO<sub>3</sub>)<sub>6</sub> (0.4 mmol, 1 equiv.) and 66 mg BDC (0.4 mmol, 1 equiv.) were added into the above mixture. The mixture was stirred for 15 min at 60 °C. The resultant solid was isolated by centrifugation and washed with water once and DMF twice. To remove the template, the as-synthesized sample was soaked in DMF for one day and ethanol for two days at 60 °C, during which time ethanol was changed every day. Finally, the product was dried overnight at 60 °C under vacuum.

### **S1.4 Instruments and methods**

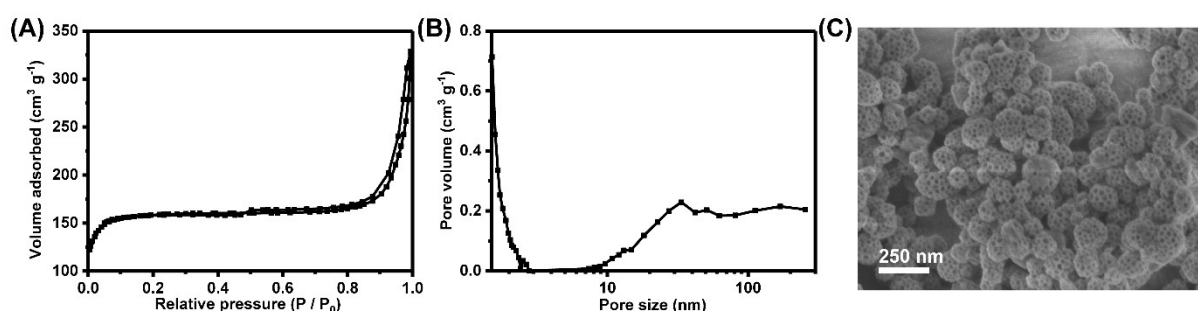
The powder X-ray diffraction (XRD) patterns were obtained on a Bruker D8 instrument using Cu K $\alpha$  radiation (40 kV, 40 mA). The Field emission scanning electron microscopy (FESEM) was conducted on Hitachi S-4800. Transmission electron microscopy (TEM) was conducted on a JEM-2100F electron microscope. N<sub>2</sub> sorption isotherms were recorded by a surface area and pore size analyzer (Micromeritics Tristar 3020). All samples were degassed under vacuum at 120 °C for 12 h before the analysis. The specific surface area was calculated using Brunauer-Emmett-Teller (BET) method using adsorption-branch data at a relative pressure (P/P<sub>0</sub>) lower than 0.15. FTIR spectra was measured by a Nicolet 7000-C spectrometer with a resolution of 4 cm<sup>-1</sup> using the KBr disc method. X-ray photoelectron spectroscopy (XPS) signals were collected on a Thermo Scientific K-Alpha spectrometer. Thermogravimetric analysis (TGA)-

differential scanning calorimetry (DSC) profiles were recorded on a Netzsch STA 449F5 by heating the sample to 500 °C in air (10 mL min<sup>-1</sup>) at a heating rate of 10 °C min<sup>-1</sup>. <sup>1</sup>H nuclear magnetic resonance (<sup>1</sup>H NMR) spectra were carried out with a Bruker Avance III 400. Prior to <sup>1</sup>H NMR measurement, samples were dried overnight at 120 °C under vacuum and then digested in 1M NaOH in D<sub>2</sub>O solution at 80 °C. After the digestion, the inorganic component was removed by centrifugation and the supernatant was transferred into an NMR tube. The elemental analysis was conducted on Elementar Unicube in CHNS mode.

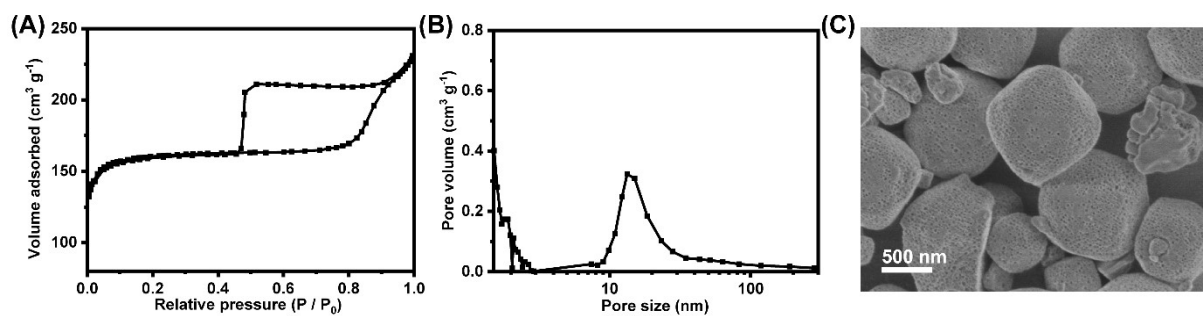
## S2. Characterizations



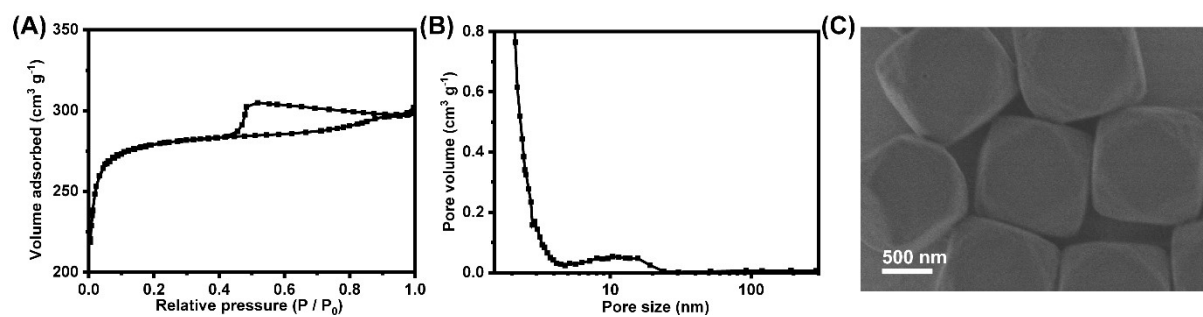
**Fig. S1** XRD patterns of HP-UiO-Ce synthesized by  $\text{PEO}_{117}\text{-}b\text{-PS}_{50}$  with (a) 0, (b) 3.4 and (c) 5.1 equiv. AA with respect to  $\text{Ce}^{4+}$ .



**Fig. S2** (A)  $\text{N}_2$  sorption isotherm, (B) its corresponding BJH pore distribution and (C) the SEM image of HP-UiO-Ce synthesized with 0 equiv. AA with respect to  $\text{Ce}^{4+}$ .



**Fig. S3.** (A)  $N_2$  sorption isotherm, (B) its corresponding BJH pore distribution and (C) the SEM image of HP-UiO-Ce synthesized with 3.4 equiv. AA with respect to  $Ce^{4+}$ .

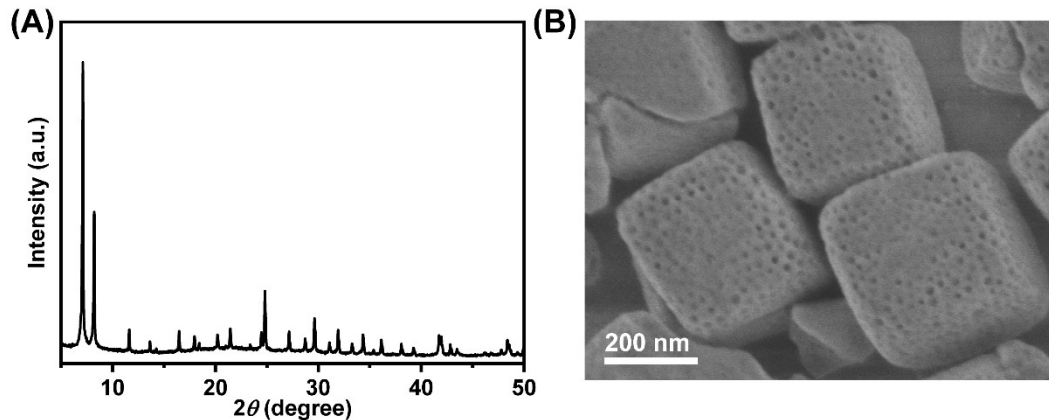


**Fig. S4** (A)  $N_2$  sorption isotherm, (B) its corresponding BJH pore distribution and (C) the SEM image of HP-UiO-Ce synthesized with 5.1 equiv. AA with respect to  $Ce^{4+}$ .

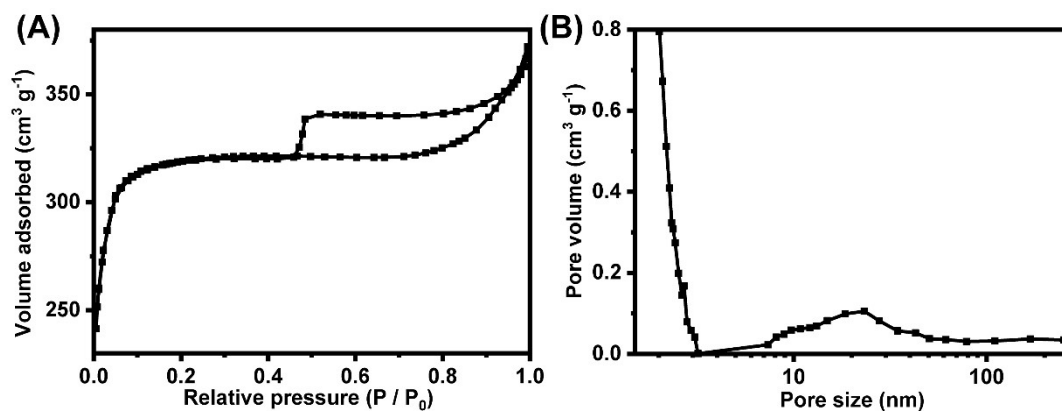
**Table S1** Detailed textural parameters for the as-synthesized HP-UiO-Ce with different amounts of AA as the modulator.

AA <sup>[a]</sup> (equiv.)	$S_{\text{BET}}$ ( $\text{m}^2 \text{g}^{-1}$ )	$S_{\text{BET-meso}}$ ( $\text{m}^2 \text{g}^{-1}$ )	$V_{\text{p}}$ ( $\text{cm}^3 \text{g}^{-1}$ )	$D_{\text{BJH}}$ (nm)
0	622	70	0.51	33 <sup>[b]</sup>
1.7	886	143	0.57	15.1
3.4	625	68	0.36	13.3
5.1	1089	124	0.46	-

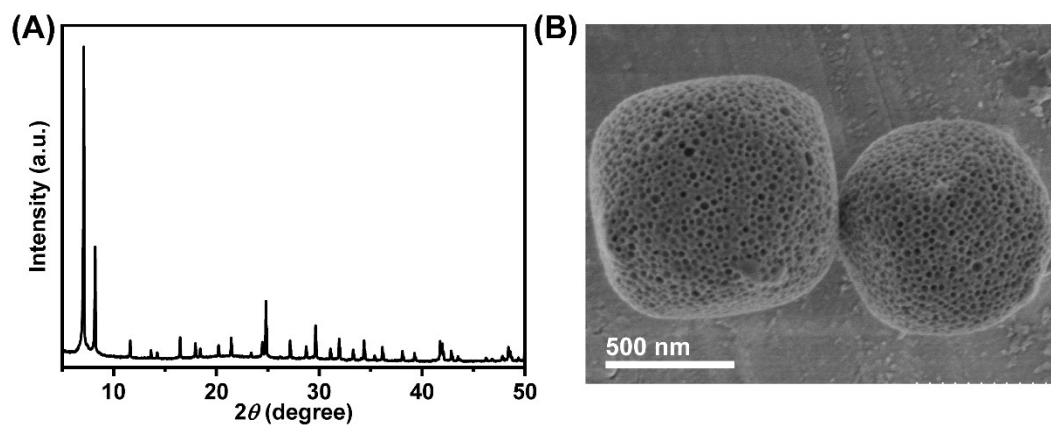
[a] The equivalents of AA added are given with respect to  $\text{Ce}^{4+}$ . [b] The broadened pore size was assigned to the interparticle spaces.



**Fig. S5** (A) The XRD pattern and (B) the typical SEM image of HP-UiO-Ce synthesized in the absence of  $\text{ClO}_4^-$ .

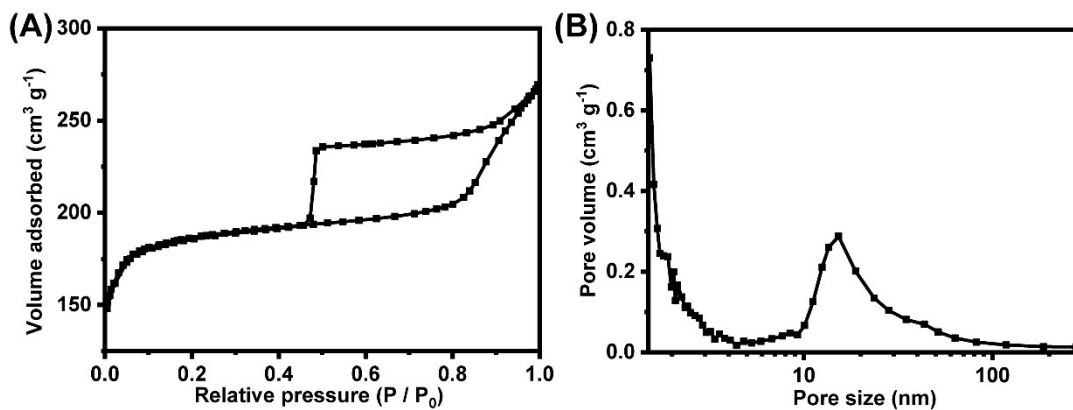


**Fig. S6** (A) N<sub>2</sub> sorption isotherm and (B) its corresponding BJH pore distribution of HP-UiO-Ce synthesized without the salting-in ion of ClO<sub>4</sub><sup>-</sup>.



**Fig. S7** (A) The XRD pattern and (B) the typical SEM image of HP-UiO-Ce synthesized with 1.4 equiv. ClO<sub>4</sub><sup>-</sup> with respect to Ce<sup>4+</sup>.



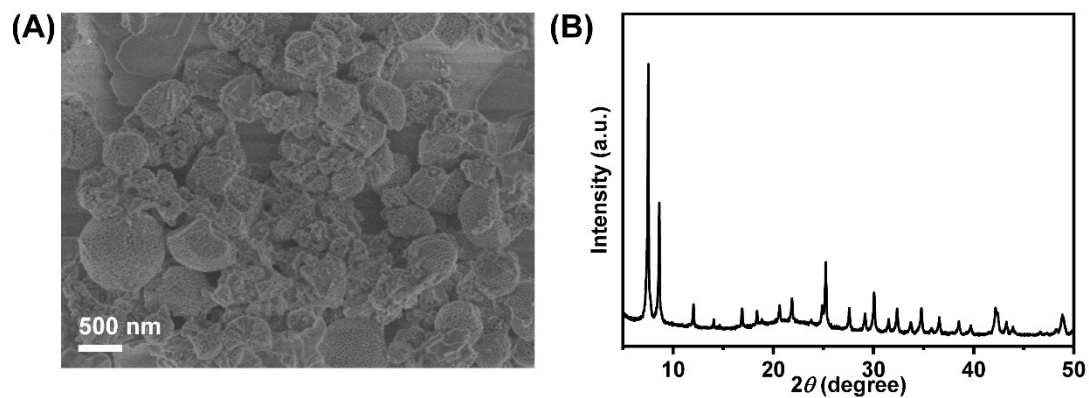


**Fig. S8** (A) N<sub>2</sub> sorption isotherm and (B) its corresponding BJH pore distribution of HP-UiO-Ce synthesized with 1.4 equiv. ClO<sub>4</sub><sup>-</sup> with respect to Ce<sup>4+</sup>.

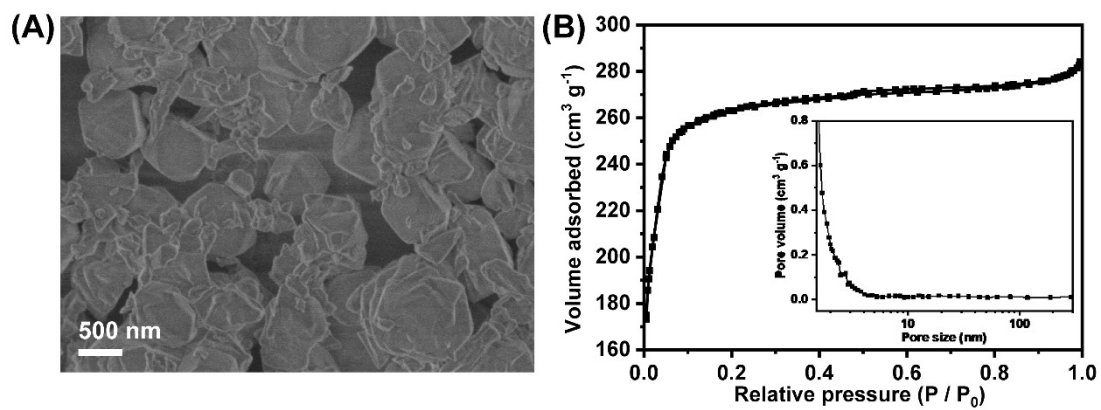
**Table S2** Detailed textural parameters for the as-synthesized HP-UiO-Ce with different amounts of salting-in ion of ClO<sub>4</sub><sup>-</sup>.

ClO <sub>4</sub> <sup>-</sup> [a] (equiv.)	S <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> )	S <sub>BET-meso</sub> (m <sup>2</sup> g <sup>-1</sup> )	S <sub>BET-micro</sub> (m <sup>2</sup> g <sup>-1</sup> )	V <sub>p</sub> (cm <sup>3</sup> g <sup>-1</sup> )	V <sub>p-micro</sub> (cm <sup>3</sup> g <sup>-1</sup> )	D <sub>BJH</sub> (nm)
0	1261	123	1138	0.57	0.44	23.1
0.7	886	143	743	0.57	0.30	15.1
1.4	723	115	608	0.42	0.24	14.8

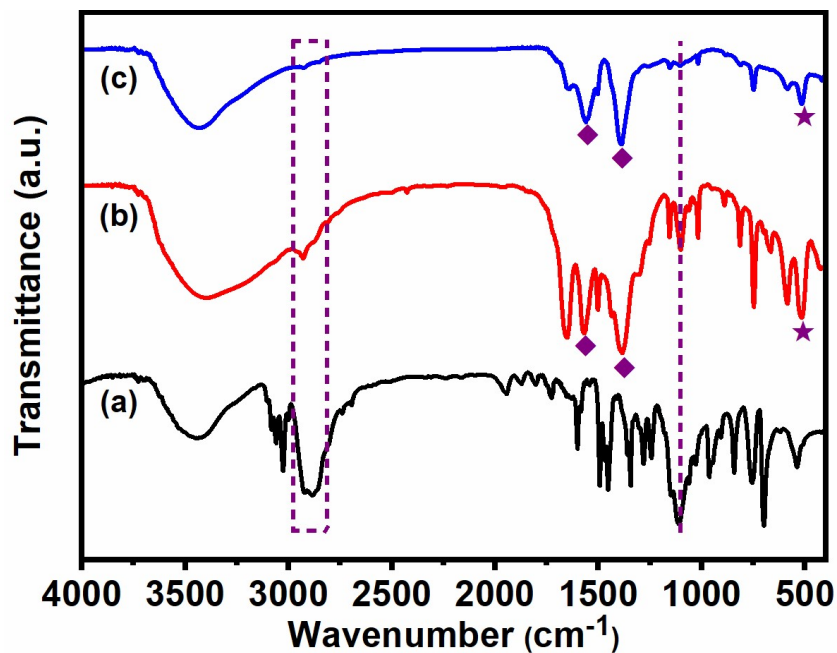
[a] The equivalents of ClO<sub>4</sub><sup>-</sup> added are given with respect to Ce<sup>4+</sup>.



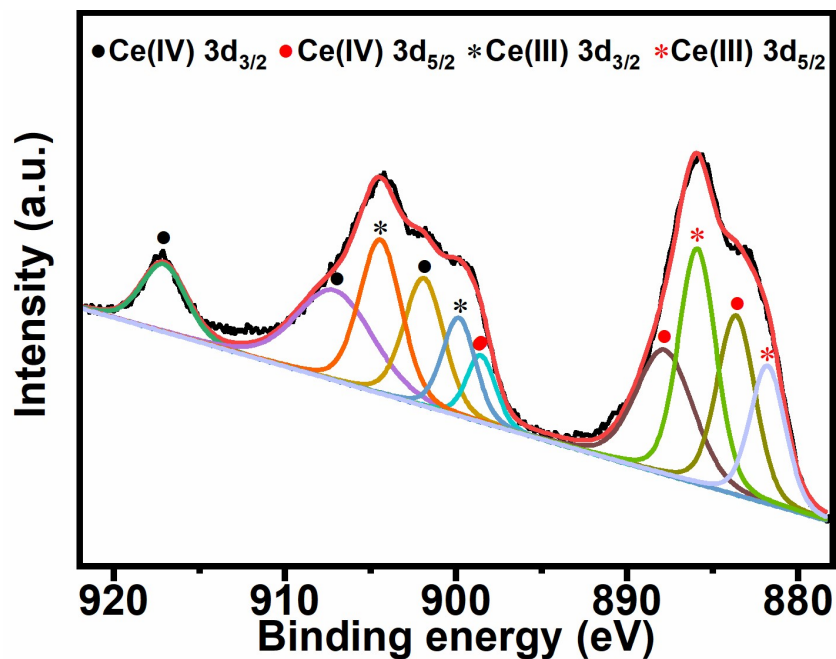
**Fig. S9** (A) The typical SEM image and (B) XRD pattern of HP-UiO-Ce synthesized with THF/H<sub>2</sub>O volume ratio of 1/8.



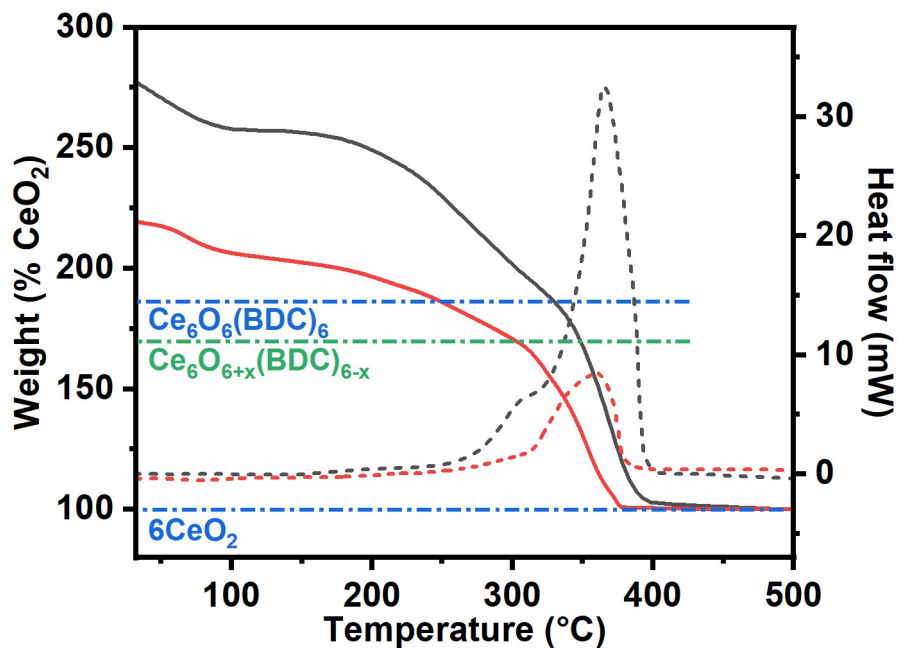
**Fig. S10** (A) The typical SEM image and (B) the N<sub>2</sub> sorption isotherm and its corresponding pore size distribution (inset) of HP-UiO-Ce synthesized with THF/H<sub>2</sub>O volume ratio of 4/8.



**Fig. S11** FT-IR spectra of (a) PEO<sub>117</sub>-*b*-PS<sub>50</sub>, (b) the as-synthesized HP-UiO-Ce and (c) extracted HP-UiO-Ce. The broad bands at 2850-2930 cm<sup>-1</sup> are assigned to the C-H vibrations of PS blocks and the band at 1109 cm<sup>-1</sup> confirms C-O-C ether groups of PEO blocks.<sup>1</sup> The peaks at 1560 and 1385 cm<sup>-1</sup> (diamonds) are attributed to the antisymmetric and symmetric stretching vibrations of carboxylate groups. The bands at 517 cm<sup>-1</sup> (stars) could be assigned to the stretching vibration of Ce-O.<sup>2</sup>

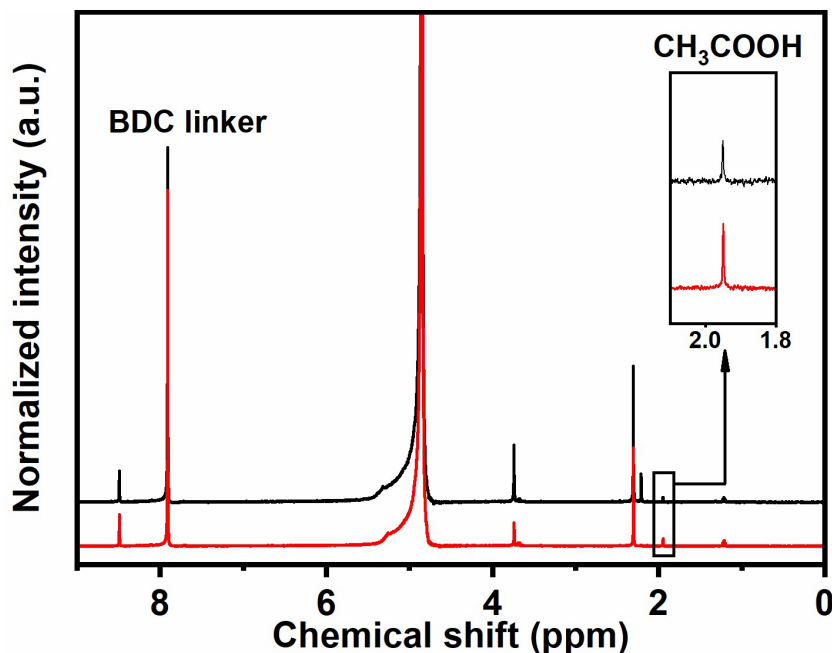


**Fig. S12** The Ce 3d XPS spectrum for the sample of HP-UiO-Ce. The binding energies at 917.2, 907.3 and 901.9 eV (black dots) correspond to the core hole 3d<sub>3/2</sub> of Ce(IV), and the peaks at 898.6, 887.9, 883.7 eV (red dots) correspond to the spin-orbit split 3d<sub>5/2</sub> of Ce(IV). The peaks at 904.4 and 899.9 eV (black asterisks) are ascribed to the core hole 3d<sub>3/2</sub> of Ce(III), and the peaks at 885.9, and 881.8 eV (red asterisks) correspond to the spin-orbit split 3d<sub>5/2</sub> of Ce(III).<sup>3</sup>



**Fig. S13** TGA profiles (solid lines) and DSC traces (dotted lines) of the as-synthesized (black) and extracted (red) HP-UiO-Ce templated by PEO<sub>117</sub>-*b*-PS<sub>50</sub>.

**Explanation for Fig. S13:** For convenience, the residue is assumed to be pure CeO<sub>2</sub> and the end weight is normalized to 100% (bottom blue horizontal chain line). The upper blue chain line pinpoints the position of the theoretical TGA plateau of the dehydroxylated ideal Ce<sub>6</sub>O<sub>6</sub>(BDC)<sub>6</sub> (=186.06%). The first step is assigned to the loss of residue ethanol and adsorbed H<sub>2</sub>O (25-100 °C). The weight loss in the range of 100-300 °C is due to the removal of AA and the dehydroxylation of the Ce-oxo clusters. The decomposition of the framework occurs at 300 °C. The green chain line represents the position of the experimental TGA plateau of the dehydroxylated HP-UiO-Ce (Ce<sub>6</sub>O<sub>6+x</sub>(BDC)<sub>6-x</sub>=170.64%). Therefore, the number of linker deficiencies per Ce<sub>6</sub> formula unit *x* is determined to be approximately 1.07. Considering the decomposition of the PEO<sub>117</sub>-*b*-PS<sub>50</sub> template in the air,<sup>4</sup> the as-synthesized HP-UiO-Ce presents a remarkable exothermic reaction and a higher complete decomposition temperature than the extracted HP-UiO-Ce sample.



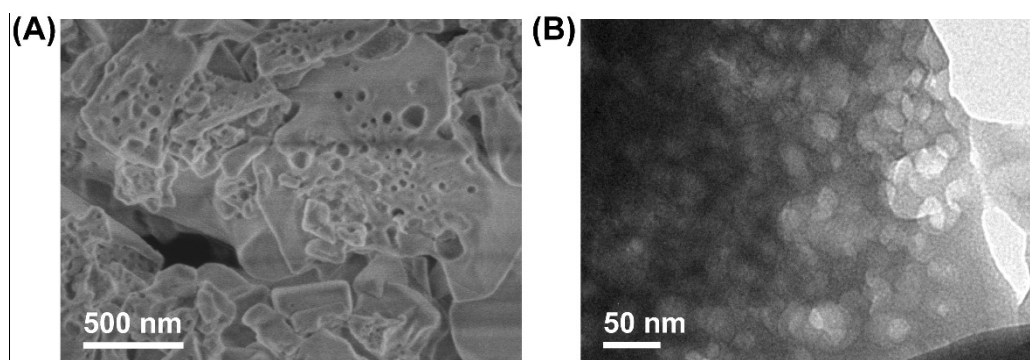
**Fig. S14** The  $^1\text{H}$  NMR spectra for the as-synthesized (black) and extracted (red) HP-UiO-Ce.

**Explanation for Fig. S14:** The spectra have been normalized to the intensity of BDC linker signal (7.9 ppm). Prior to NMR analysis, HP-UiO-Ce samples were heated to 120 °C (the boiling point of AA is 118 °C) and then digested by basic NaOH/D<sub>2</sub>O solution. It is worth noting that DMF originating from the washing procedure remains in the samples due to its high boiling point (153 °C). Thus, formate (8.5 ppm) and dimethylamine (2.3 ppm), products of the base catalyzed DMF hydrolysis, were observed.<sup>5</sup> The intensity of the acetic (1.9 ppm) from AA modulator (inset) does not change obviously before and after the washing procedure, and thus we conclude that all the residual acetate is incorporated into MOFs to compensate for BDC linker deficiencies. Considering the similar temperature ranges of dehydroxylation and AA modulator loss, the suitable molecular formula for the hydroxylated sample is  $\text{Ce}_6\text{O}_{4+2x-2y}(\text{OH})_{4-2x+2y}(\text{BDC})_{6-x}(\text{CH}_3\text{COO})_{2y}$  (x represent the number of linker deficiencies of per Ce<sub>6</sub> formula unit determined by TGA). In this HP-UiO-Ce, the molar ratio between AA and BDC was calculated to be 0.03, and thus y was to be 0.07.<sup>5</sup> The calculated composition is  $\text{Ce}_6\text{O}_6(\text{OH})_2(\text{BDC})_{4.93}(\text{CH}_3\text{COO})_{0.14}$ , describing that carboxylate sites are occupied by 0.14 AA modulator molecules 9.86 BDC linkers in average Ce<sub>6</sub> cluster.

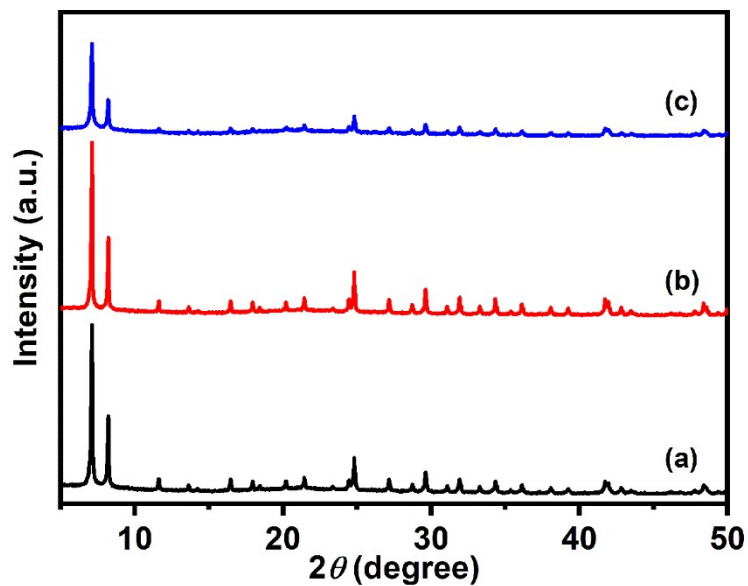
**Table S3** The Ce, C, and N elemental content for the as-synthesized and extracted HP-UiO-Ce.

Sample	Ce (wt%) <sup>[a]</sup>	C (wt%) <sup>[b]</sup>	N (wt%) <sup>[b]</sup>	C/Ce <sup>[c]</sup>
As-synthesized HP-UiO-Ce	27.88	27.62	2.76	0.74
Extracted HP-UiO-Ce	35.49	26.29	1.57	0.63

[a] The Ce content was determined by ICP-OES. [b] The C and N content was measured by organic elemental analysis. [c] The weight ratio between C and Ce excludes the C content in DMF but includes the C content in frameworks, AA modulators, and ethanol.



**Fig. S15** (A) The typical SEM image and (B) TEM image of HP-UiO-Ce synthesized with PEO<sub>117</sub>-*b*-PS<sub>150</sub> as the template.

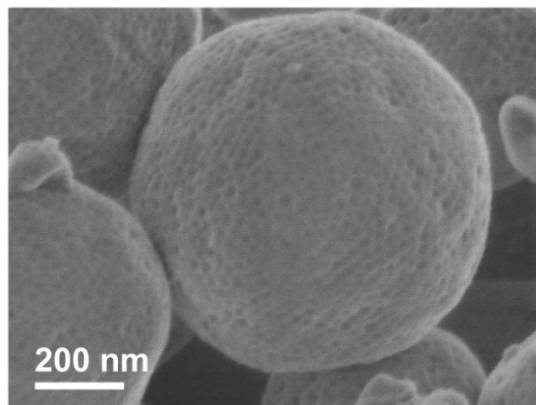


**Fig. S16** XRD patterns of HP-UiO-Ce synthesized with TMB/PEO-*b*-PS weight ratio of (a) 0.10, (b) 0.24 and (c) 0.29.

**Table S4** Detailed textural parameters for the as-synthesized HP-UiO-Ce with different weight ratios of TMB/PEO-*b*-PS.

TMB/PEO- <i>b</i> -PS (wt %)	$S_{\text{BET}}$ ( $\text{m}^2 \text{g}^{-1}$ )	$S_{\text{BET-meso}}$ ( $\text{m}^2 \text{g}^{-1}$ )	$V_{\text{p}}$ ( $\text{cm}^3 \text{g}^{-1}$ )	$D_{\text{BJH}}$ (nm)
0.10	1177	174	0.56	17.1
0.24	1118	165	0.58	23.4
0.29	1098	194	0.50	-





**Fig. S17** The typical SEM image of HP-UiO-Ce with TMB/PEO-*b*-PS weight ratio of 0.29.

### S3. References

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