

## Supplementary information

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# Creating hierarchical pores in metal–organic frameworks via postsynthetic reactions

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## SUPPLEMENTARY INFORMATION

### Creating Hierarchical Pores in Metal–Organic Frameworks via Post-Synthetic Reactions

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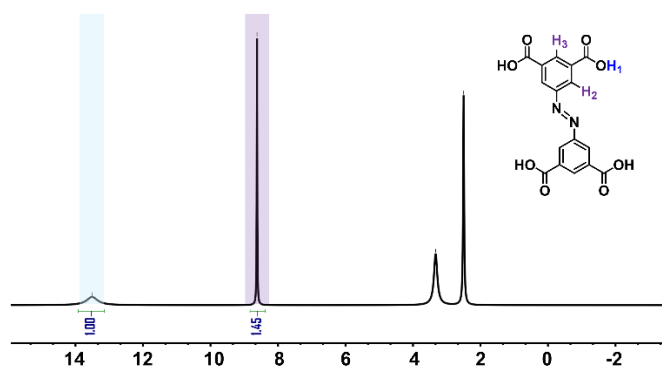
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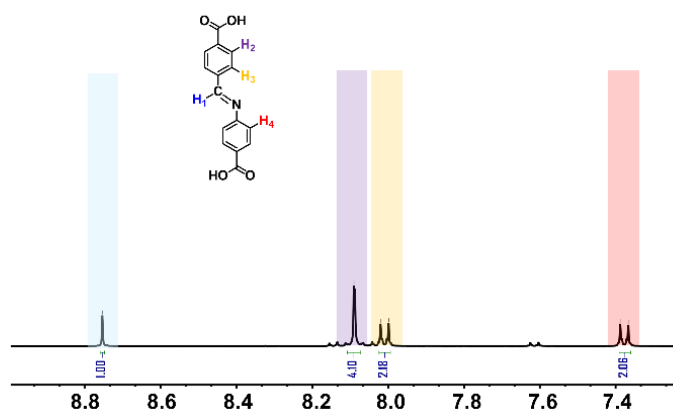
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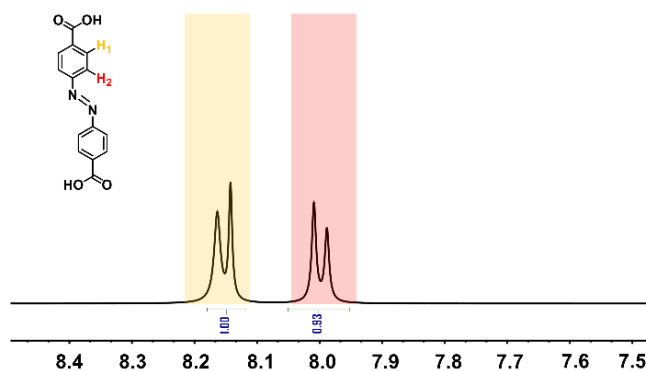
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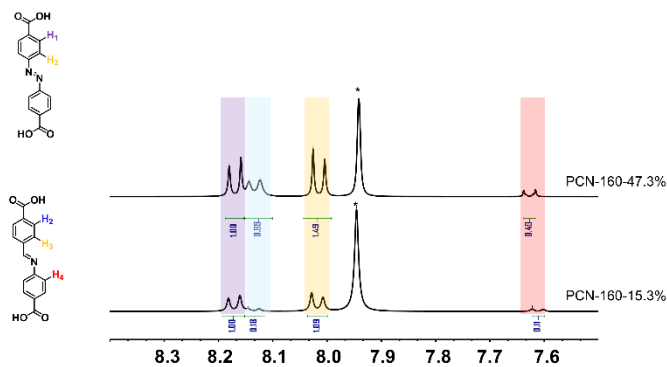
**Supplementary Figure 1** |  $^1\text{H}$  NMR spectrum of the  $\text{H}_4\text{ABTC}$  in  $\text{DMSO-}d_6$ . Note that the chemical shifts of  $\text{H}_2$  and  $\text{H}_3$  are too close to be distinguished. The peaks at 2.5 and 3.3 can be attributed to  $\text{DMSO}$  and  $\text{DMSO-}d_6$ , respectively.



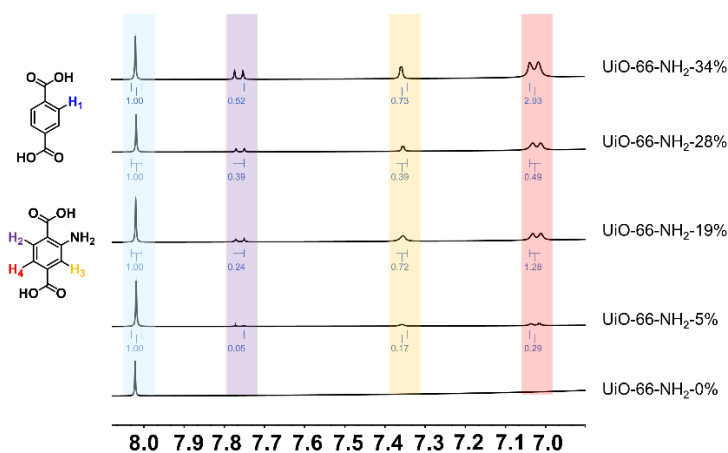
**Supplementary Figure 2** |  $^1\text{H}$  NMR spectrum of  $\text{H}_2\text{CBAB}$  in  $\text{DMSO-}d_6$ .



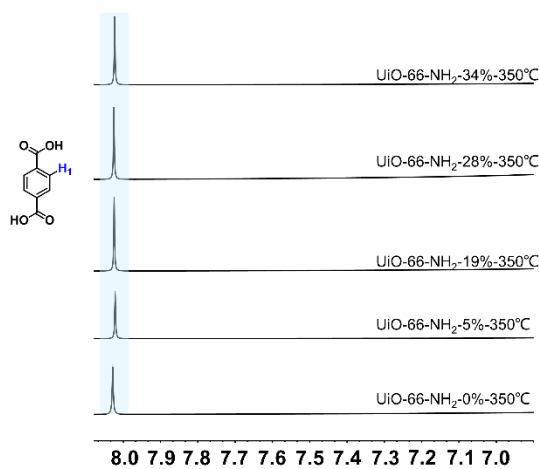
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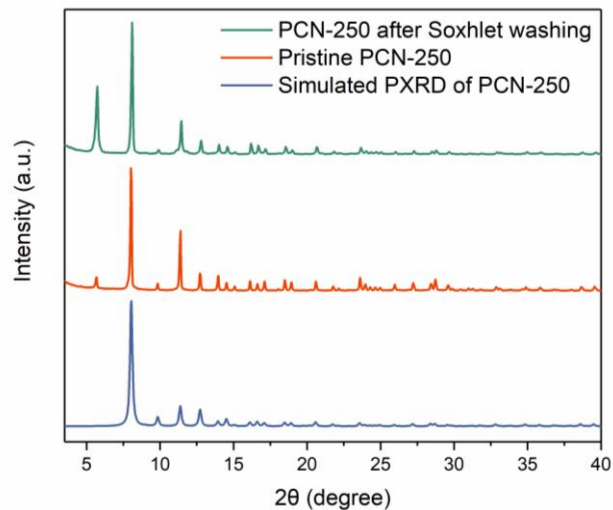
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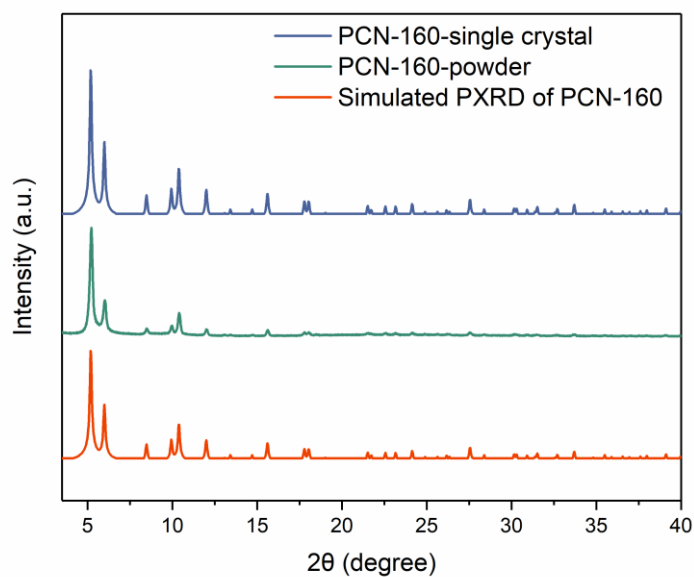
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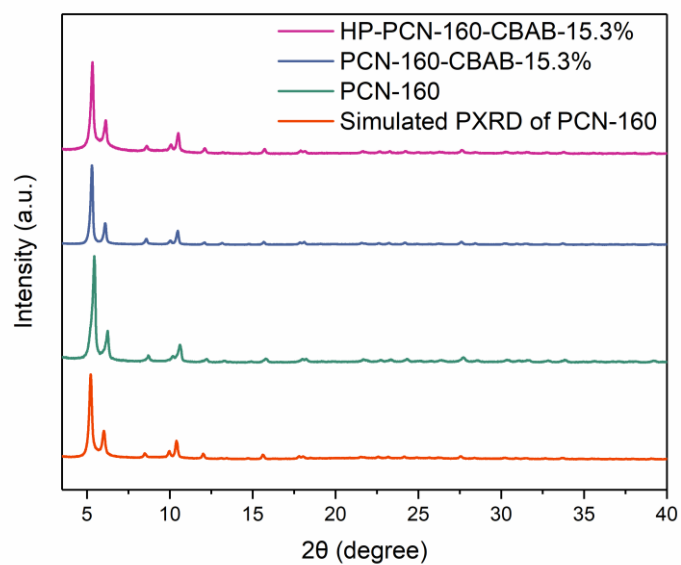
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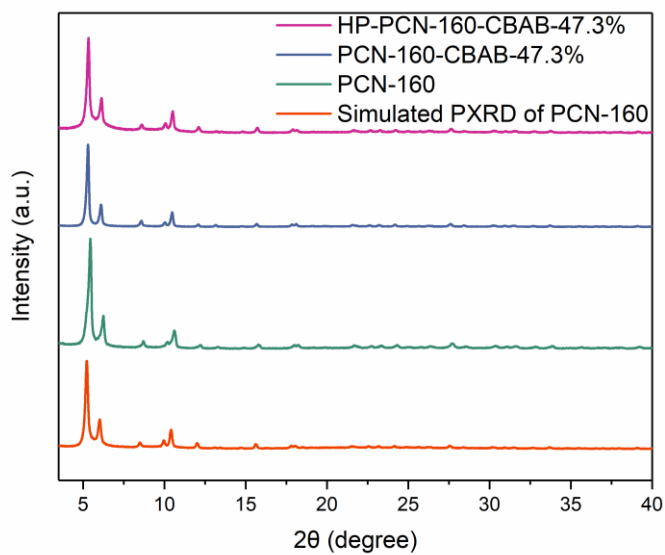
**Supplementary Figure 7** | Powder X-ray diffraction results of the PCN-250 before and after Soxhlet washing. The data was collected on a Bruker Advance D8 powder X-ray diffractometer. a.u. represents arbitrary units.



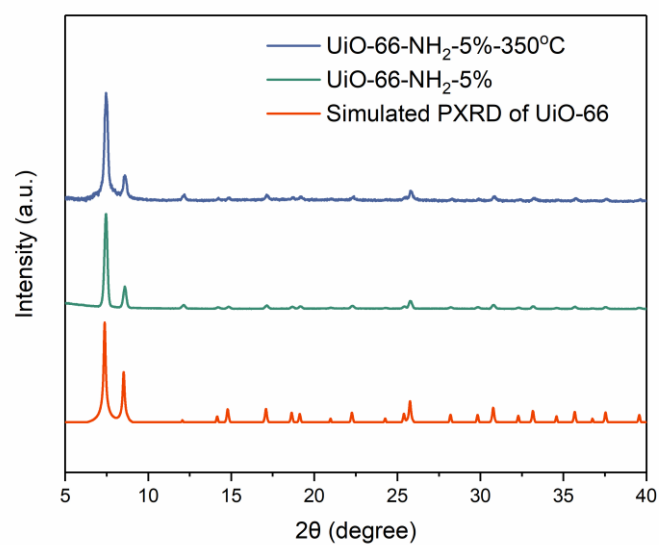
**Supplementary Figure 8** | Powder X-ray diffraction results of the PCN-160 powder and single crystals.



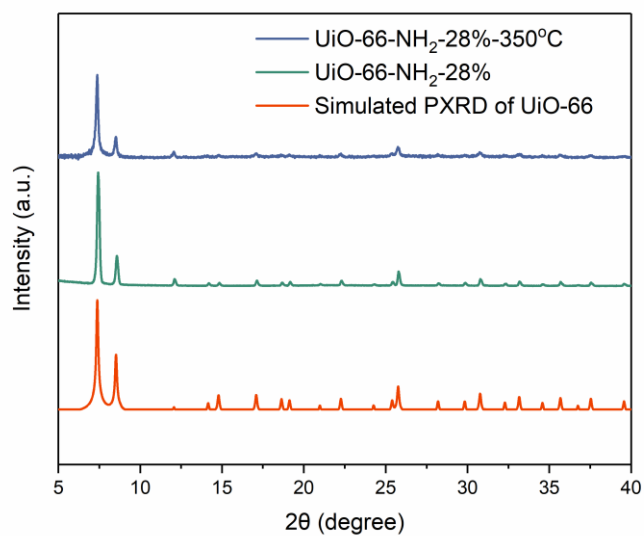
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**Supplementary Figure 10** | Powder X-ray diffraction results of the PCN-160-CBAB-47.3% before and after linker hydrolysis.

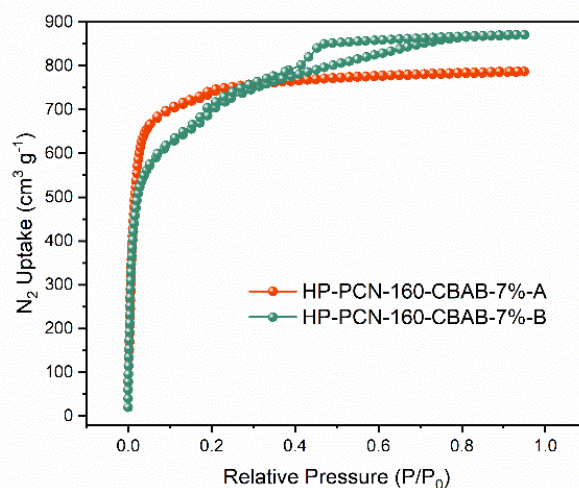


**Supplementary Figure 11** | Powder X-ray diffraction results of the UiO-66-NH<sub>2</sub>-5% before and after treatment under 350°C.

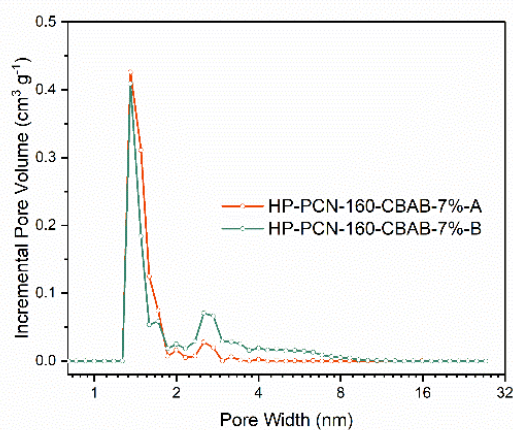


**Supplementary Figure 12** | Powder X-ray diffraction results of the UiO-66-NH<sub>2</sub>-28% before and after treatment under 350°C.

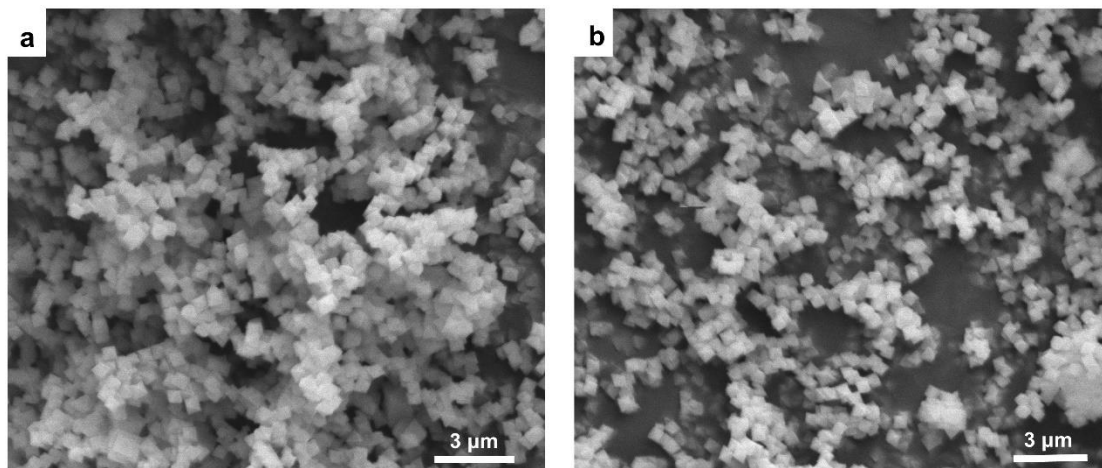




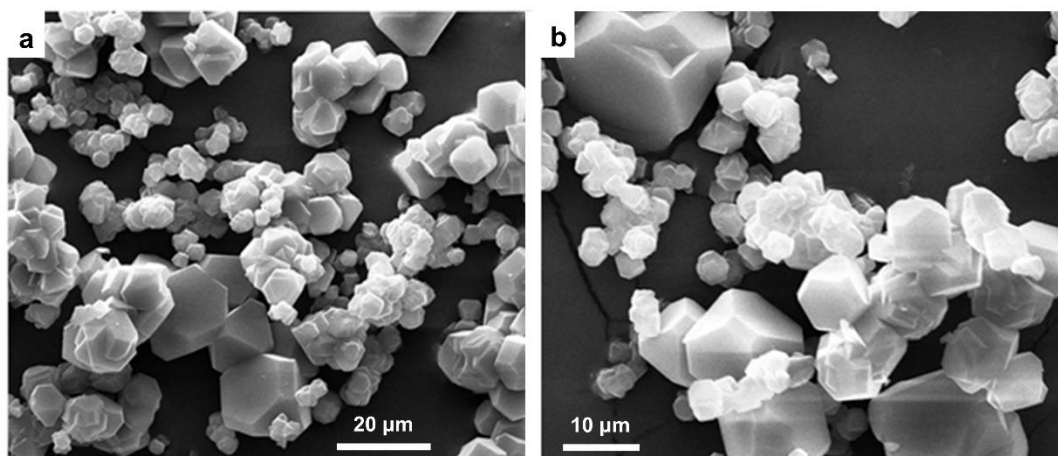
**Supplementary Figure 13** | Nitrogen sorption isotherms of the hierarchically porous (HP) PCN-160-CBAB-7% that are (A) washed with acetone at room temperature and (B) washed with acetone at 40°C.



**Supplementary Figure 14** | Pore size distribution of the hierarchically porous (HP) PCN-160-CBAB-7% that are (A) washed with acetone at room temperature and (B) washed with acetone at 40°C.



**Supplementary Figure 15** | SEM images of (a) UiO-66-NH<sub>2</sub>-28% and (b) UiO-66-NH<sub>2</sub>-28%-350°C.



**Supplementary Figure 16** | SEM images of (a) pristine PCN-250 and (b) PCN-250 after Soxhlet washing.

**Supplementary Table 1** | Porosity analysis of hierarchically porous MOFs reported in the protocol.

MOF	$S_{\text{BET}}$ ( $\text{m}^2 \text{g}^{-1}$ ) <sup>A</sup>	$D_{\text{meso}}$ (nm) <sup>B</sup>	$V_{\text{meso}}/V_{\text{micro}}$ <sup>C</sup>
PCN-250 after Soxhlet washing	1416	6.7	0.099
HP-PCN-160-CBAB-0%	2704	2.5	0.036
HP-PCN-160-CBAB-15.3%	1988	6.0	1.51
HP-PCN-160-CBAB-47.3%	714	14.0	7.55
UiO-66-NH <sub>2</sub> -0%-350°C	1327	-	0
UiO-66-NH <sub>2</sub> -5%-350°C	902	3.5	1.15
UiO-66-NH <sub>2</sub> -19%-350°C	818	3.9	1.24
UiO-66-NH <sub>2</sub> -28%-350°C	780	4.7	1.67
UiO-66-NH <sub>2</sub> -34%-350°C	890	3.5	1.27