

Supporting Information

Template mediated and solvent-free route to a variety of UiO-66 Metal-Organic Frameworks

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Experimental Section

Materials. All chemicals and solvents were purchased from commercial sources and were used without additional purification. The purities of the chemicals used in this work are as followings: 1,4-benzenedicarboxylic acid (98%, Sigma-Aldrich), $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (98%, Sigma-Aldrich), ZrCl_4 (99.5%, Sigma-Aldrich), tetraethylammonium bromide (98%, Aldrich), tetramethylammonium bromide (98%, Sigma-Aldrich), tetrapropylammonium bromide (98%, Aldrich), N,N-Dimethylformamide (99.9%, Sigma-Aldrich), HCl (37% aq, Sigma-Aldrich).

Characterization. ATR-IR were recorded on a Bruker VERTEX 70 using a Bruker Platinum ATR unit. Thermogravimetric analysis (TGA) was carried out on a Texas Instruments TGA-Q5000 with a heating rate of $10\text{ }^\circ\text{C min}^{-1}$. N_2 adsorption and desorption isotherms were obtained by using Quantachrome Nova 4000e sorption apparatus. (The samples were activated by refluxing in MeOH overnight, filtrated and vacuum dried at $200\text{ }^\circ\text{C}$ for 12 h before test.) Powder X-ray diffraction (PXRD) was performed on a STOE STADI P system with an IP-PSD or a DECTRIS MYTHEN 1K detector. Elemental analysis were measured at the Laboratory for Microanalytics at the Institute of Inorganic Chemistry at Technische Universität München. Heating setups for parallel experiments were performed with programmable Barker thermoblock or programmable HLC BioTech thermoblock.

Solvent-free route for UiO-66 synthesis. Optimized synthetic conditions: the mixture of BDC (1 mmol), $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (1 mmol) and TEABr (1.42 mmol) was grinded in the agate mortar for 5 min, then transferred to the ACE pressure tube before standing at 180 °C for 24 h crystallization. Pale white product (250 – 270 mg, yields varied little bit from time to time) can be obtained with nearly quantitative yield, after washing with H_2O , MeOH and Et_2O successively followed by drying under vacuum. And the method can be scaled up at least to 20 mmol without any significant difference.

Conventional solvent-thermal synthesis of UiO-66. UiO-66 can be synthesized via a modulated procedure illustrated in the literature.¹ ZrCl_4 (0.54 mmol, 126 mg) was dissolved in the mixed solvent of DMF (10 mL) and HCl (37% aq, 2 mL) in the ACE pressure tube, and sonicated for 20 min. The BDC ligand (0.76 mmol, 126 mg) in DMF (10 mL) was added afterwards. The mixture was heated at 120 °C overnight. Pale white product was gained after filtration. The UiO-66 was activated by immersing in DMF and acetone successively for 72 h (solvents were changed every 24 h). After vacuum drying for 12 h, the final product was gained as white crystalline powder (209 mg).

Elemental analysis. UiO-66 ($\text{Zr}_{24}\text{O}_{120}\text{C}_{192}\text{H}_{96}$) Calculated: C, 35.41; H, 1.49; O, 29.48; Zr, 33.62. Found: C, 31.17; H, 2.31; N 1.20 (hydrothermal synthesized). Found: C, 31.12; H, 2.40; N, 0.38 (solvent-free synthesized). Elemental analysis values for UiO-66 in the literatures are also listed in the Table S1, which also shows quite large deviation. These may derivate from residual of the solvents (such as DMF, DEF or DME used for most of time) and additives (acid or template) etc.¹ Moreover, the defects of the framework structures can also cause the deviation of the CHN values from the ideal ones of the perfect structure.

Table S1. Elemental analysis (C, H, N) values for UiO-66 in the literatures

Elemental analysis	C	H	N
HCl as the modulator ¹	31.18	2.71	1.96
Acetic acid as the modulator ¹	35.18	2.76	2.03
Calculated	35.41	1.49	--
This work (hydrothermal)	31.17	2.31	1.20
This work (solvent-free)	31.12	2.40	0.38

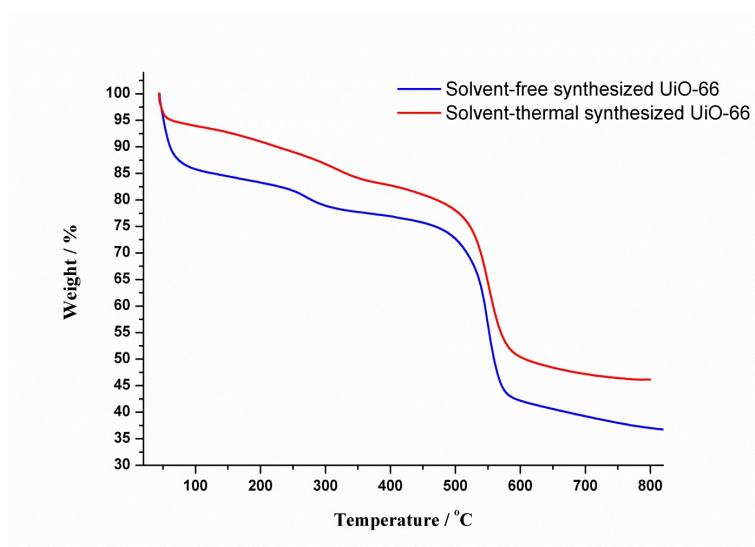


Figure S1. TGA pattern for the UiO-66 synthesized with solvent-thermal and solvent-free route respectively.

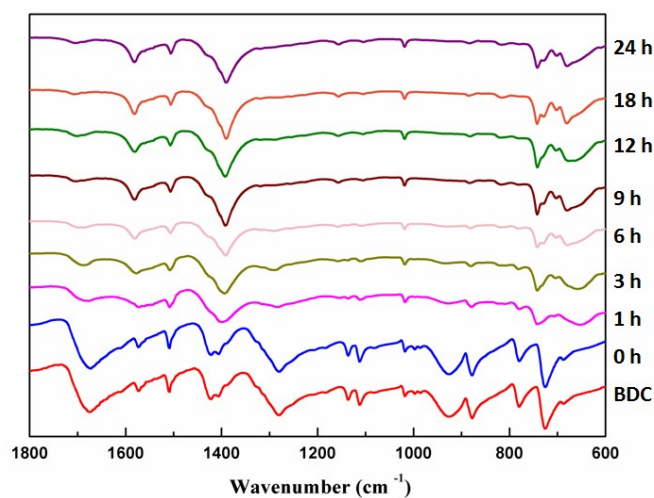


Figure S2. ATR-IR traces of UiO-66 formation process via the crystallization time

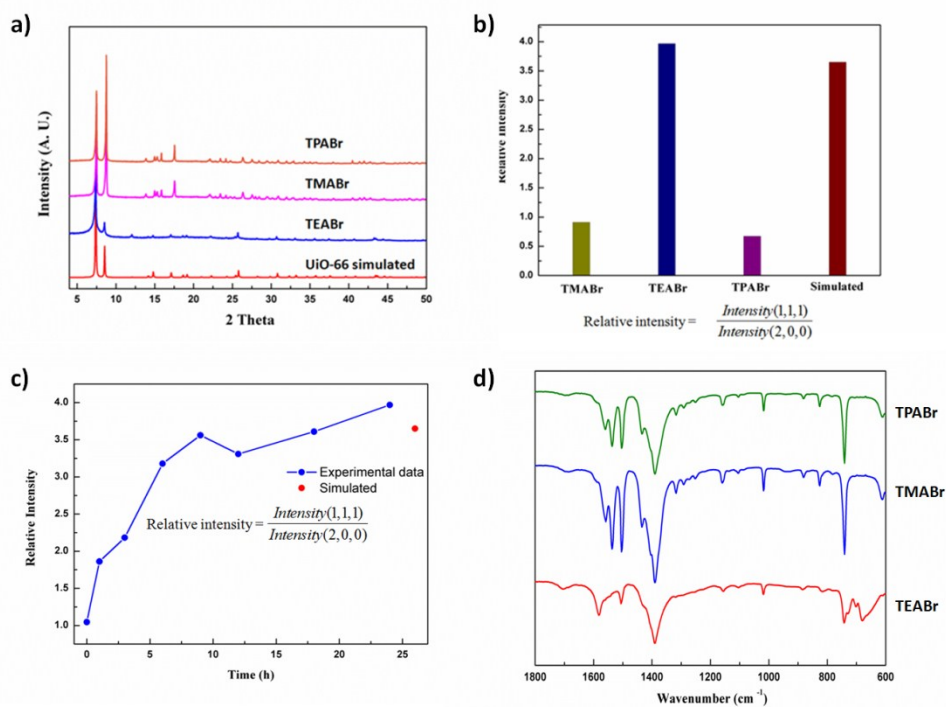


Figure S3. (a) PXRD of solvent-free synthesized UiO-66s with different quaternary ammonium salts as the templates and (b) comparison of the relative intensity of (1, 1, 1) versus (2, 0, 0) phase direction; (c) traces of relative intensity changes with crystallization time using TEABr as the template; (d) ATR-IR comparison of UiO-66s with various templates.

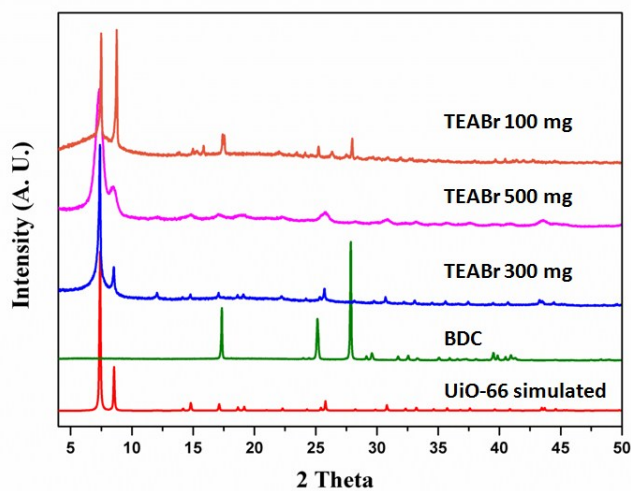


Figure S4. PXRD patterns of solvent-free synthesized UiO-66s with different amount of the template.

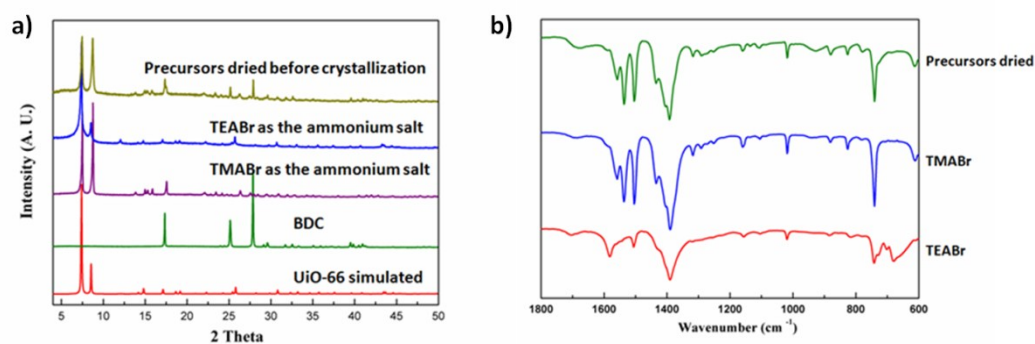


Figure S5. (a) PXRD patterns and (b) ATR-IR spectra for solvent-free synthesized UiO-66 with pre-dried precursors (TEABr as the template) and comparison with other UiO-66s without pre-dried procedure and/or with different templates.

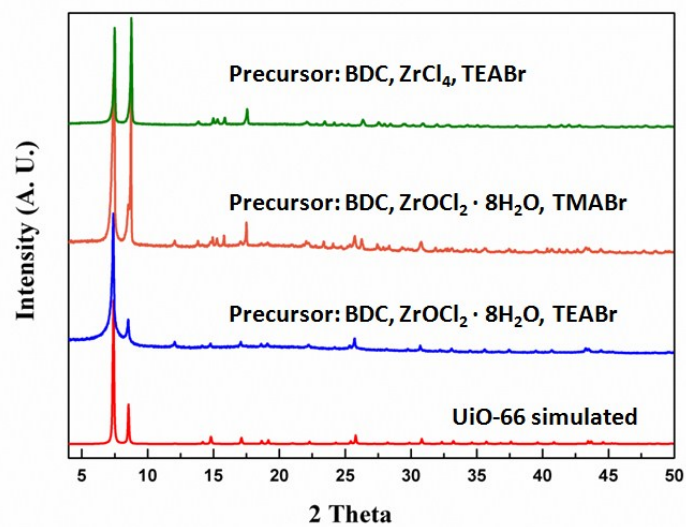


Figure S6. PXRD patterns of solvent-free synthesized UiO-66 using different precursors.

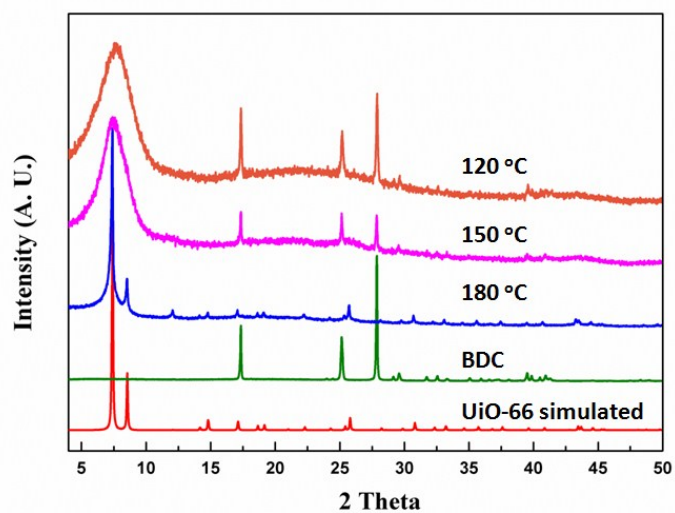


Figure S7. PXRD patterns of solvent-free synthesized UiO-66s with different crystallization temperature

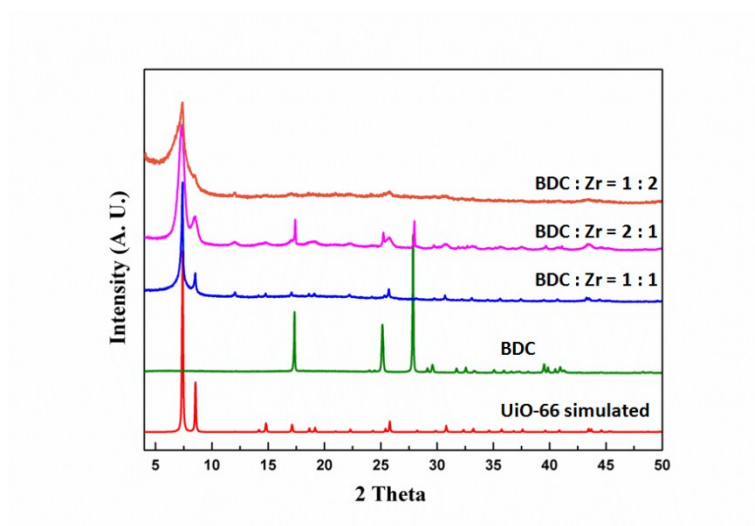


Figure S8. PXRD patterns of solvent-free synthesized UiO-66s with different BDC/Zr ratio.

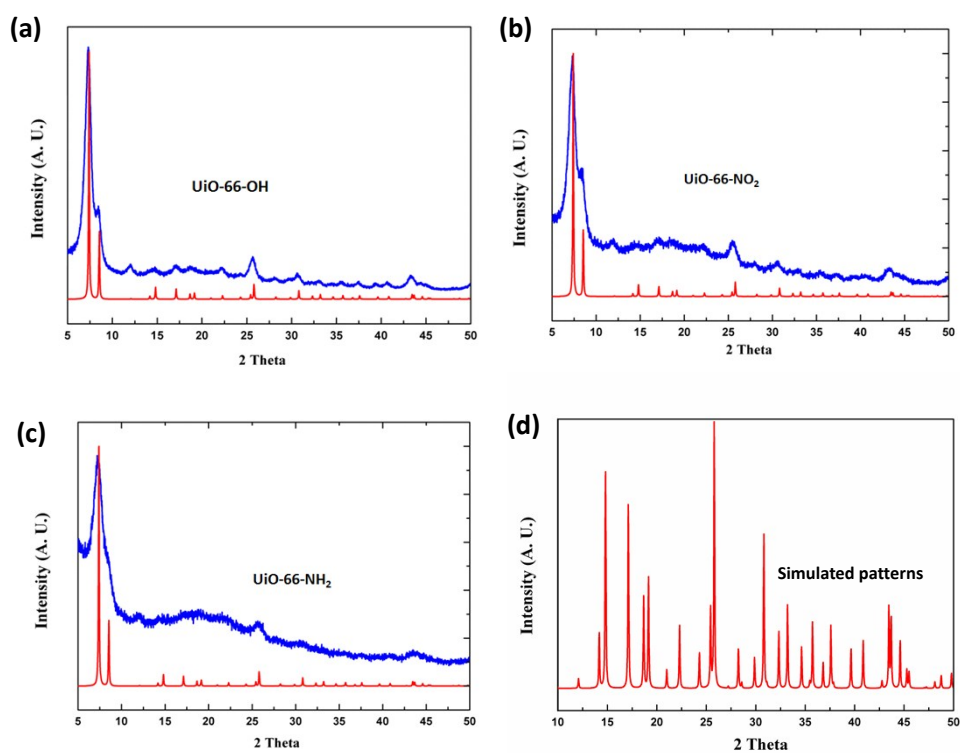


Figure S9. PXRD patterns of solvent-free synthesized UiO-66-OH, UiO-66-NO₂ and UiO-66-NH₂ (red line: simulated PXRD patterns; blue line: experimental patterns)

References:

1. M. J. Katz, Z. J. Brown, Y. J. Colón, P. W. Siu, K. A. Scheidt, R. Q. Snurr, J. T. Hupp and O. K. Farha, *Chem. Comm.*, 2013, **49**, 9449.