

**Supplementary Information**  
**Facile synthesis of morphology- and size-controlled**  
**zirconium metal-organic framework UiO-66: the role of**  
**hydrofluoric acid in crystallization**

Yitong Han<sup>a</sup>, Min Liu<sup>a</sup>, Keyan Li<sup>a</sup>, Yi Zuo<sup>a</sup>, Yingxu Wei<sup>b</sup>, Shutao Xu<sup>b</sup>, Guoliang

Zhang<sup>c</sup>, Chunshan Song<sup>ad</sup>, Zongchao Zhang<sup>b</sup> and Xinwen Guo<sup>a\*</sup>

<sup>a</sup> State key laboratory of fine chemicals, PSU-DUT Joint Center for Energy Research,  
School of Chemical Engineering, Dalian University of Technology, Dalian 116024,  
PR China

<sup>b</sup> Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics,  
Chinese Academy of Sciences, Dalian 116023, PR China

<sup>c</sup> College of Biological and Environmental Engineering, Zhejiang University of  
Technology, Hangzhou 310014, PR China

<sup>d</sup> EMS Energy Institute, PSU-DUT Joint Center for Energy Research and Department  
of Energy & Mineral Engineering, Pennsylvania State University, University Park,  
Pennsylvania 16802, USA

\* Corresponding author,E-mail: guoxw@dlut.edu.cn; Fax: +86 0411 84986134; Tel:  
+86 0411 84986133

**SEM image of UiO-66 produced by non-modulated solvothermal method**

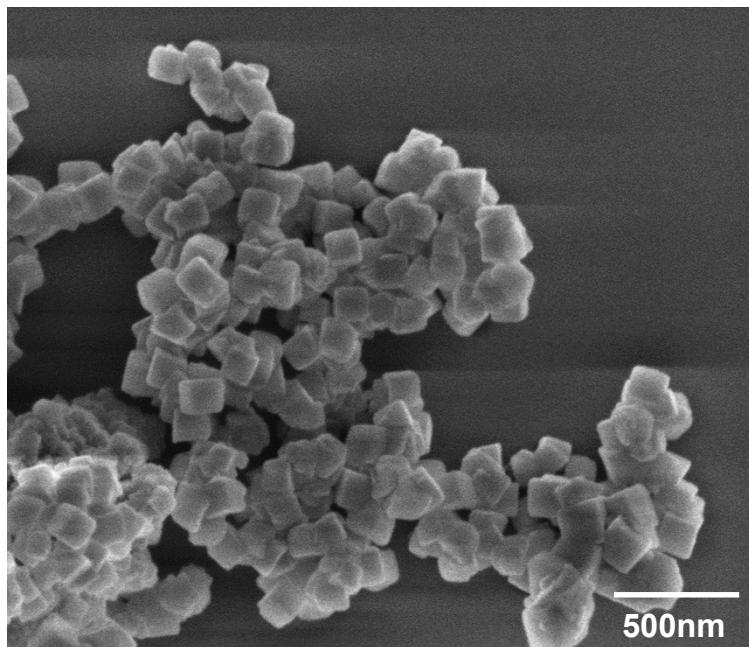


Fig. S1. SEM image of fluorine-free UiO-66.

**The specific amounts of reactants and hydrofluoric acid modulator in  
the synthesis**

Table S1 The amounts of reactants and HF modulator in the synthesis.

DMF (mL)	Concentration of reactants (mM)	ZrCl <sub>4</sub> (g)	H <sub>2</sub> BDC (g)	Eq of HF	HF (mL)
50	13.6	0.159	0.113	1	0.029
50	13.6	0.159	0.113	2	0.058
50	13.6	0.159	0.113	3	0.087
50	18.2	0.212	0.151	1	0.039
50	18.2	0.212	0.151	2	0.078
50	18.2	0.212	0.151	3	0.117
50	27.2	0.317	0.226	1	0.059
50	27.2	0.317	0.226	2	0.118
50	27.2	0.317	0.226	3	0.177

# The element analysis of fluorine-free UiO-66 and 3F-UiO-66 (UiO-66 with 3 eq HF)

Table S2 The elemental composition of fluorine-free UiO-66.

Element	Weight percentage	Atomic percentage
	(wt %)	(%)
C	51.31	67.09
O	30.16	29.61
Cl	0.40	0.18
Zr	18.13	3.12
Total	100	100

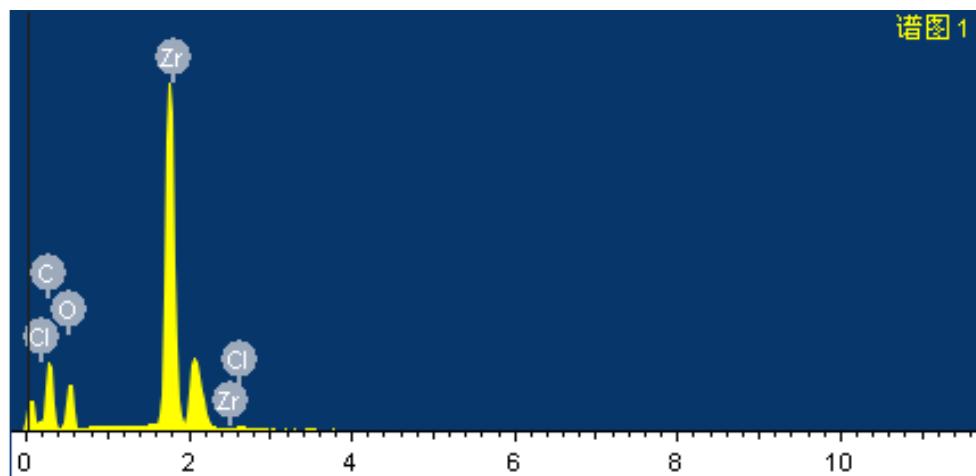


Fig. S2. EDS spectrum of fluorine-free UiO-66.

Table S3 The elemental composition of 3F-Uio-66 (C=18.2 mM).

Element	Weight percentage (wt %)	Atomic percentage (%)
C	44.75	63.17
O	25.43	26.95
F	6.14	5.48
Zr	23.68	4.40
Total	100	100

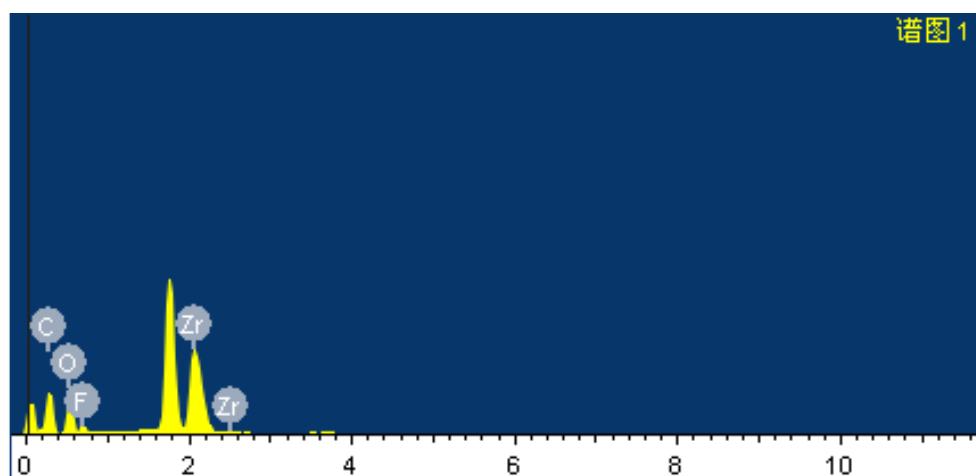


Fig. S3. EDS spectrum of 3F-Uio-66 (C=18.2 mM).

## The half-peak widths analysis

Five characteristic diffraction peaks at  $2\theta = 7.3^\circ$ ,  $8.5^\circ$ ,  $17.1^\circ$ ,  $25.8^\circ$  and  $30.8^\circ$  were chosen to measure the half-peak widths. The results are shown in Table S4.

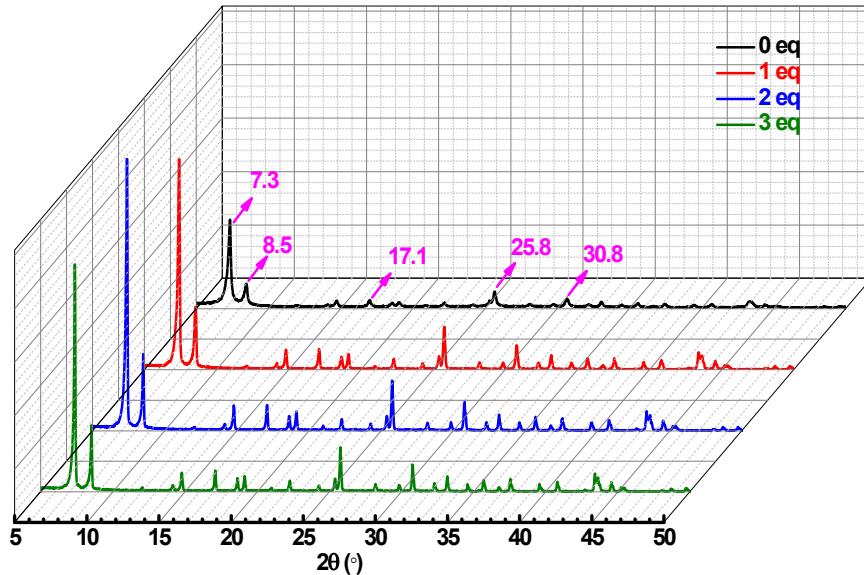


Fig. S4. XRD patterns of UiO-66 obtained with different additive amounts of hydrofluoric acid ( $C=18.2$  mM).

Table S4 The half-peak widths of the XRD patterns of UiO-66 obtained with different additive amounts of HF ( $C=18.2$  mM).

$2\theta$ ( $^\circ$ )	Eq of HF			
	0	1	2	3
7.3	0.193	0.155	0.121	0.111
8.5	0.182	0.129	0.105	0.090
17.1	0.177	0.125	0.105	0.098
25.8	0.163	0.120	0.103	0.096
30.8	0.157	0.117	0.096	0.091

## The weight-loss values (%) of fluorine-free UiO-66 and fluorine-involved UiO-66

Table S5 Comparison of weight-loss values (%) of the fluorine-free UiO-66 and fluorine-involved UiO-66 at different temperature interval.

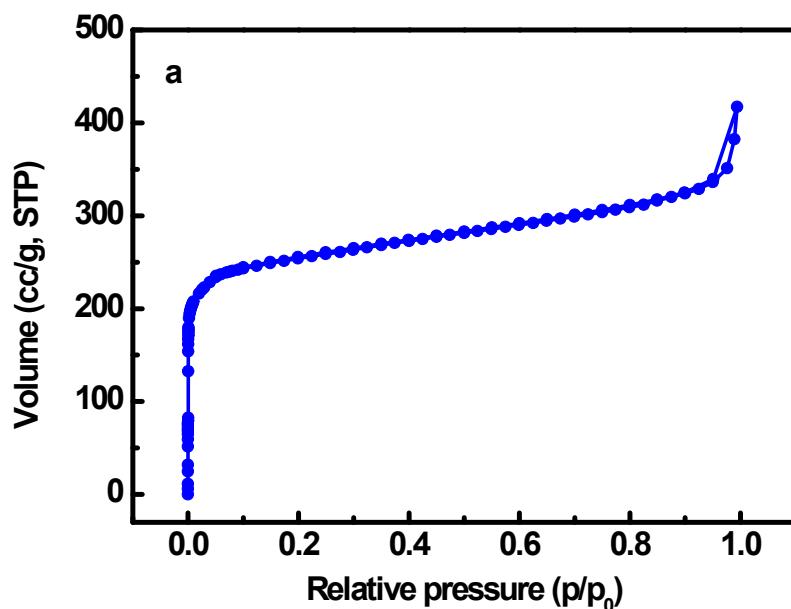
Samples	Weight-loss temperature interval (°C)				Stoichiometric <sup>a</sup> 350–750 °C	
	Measured					
	20–100	100–200	200–350	350–750		
0 F	5.52	12.80	11.30	26.92	54.6%	
1 F	4.54	13.46	7.91	27.20	—	
2 F	4.60	15.05	6.74	29.24	—	
3 F	6.26	13.39	6.18	27.46	—	

<sup>a</sup> stoichiometrically perfect framework

## The porosity data of fluorine-free UiO-66

Table S6 Sorption data of fluorine-free UiO-66.

Crystal morphology	Crystal size ( $\mu\text{m}$ )	$S_{\text{BET}}$ ( $\text{m}^2 \cdot \text{g}^{-1}$ )	$V_{\text{micro}}$ ( $\text{cm}^3 \cdot \text{g}^{-1}$ )	$V_{\text{total}}$ ( $\text{cm}^3 \cdot \text{g}^{-1}$ )	Pore size (nm)
Small cube	$\sim 0.17$	867	0.26	0.53	0.7, 0.9



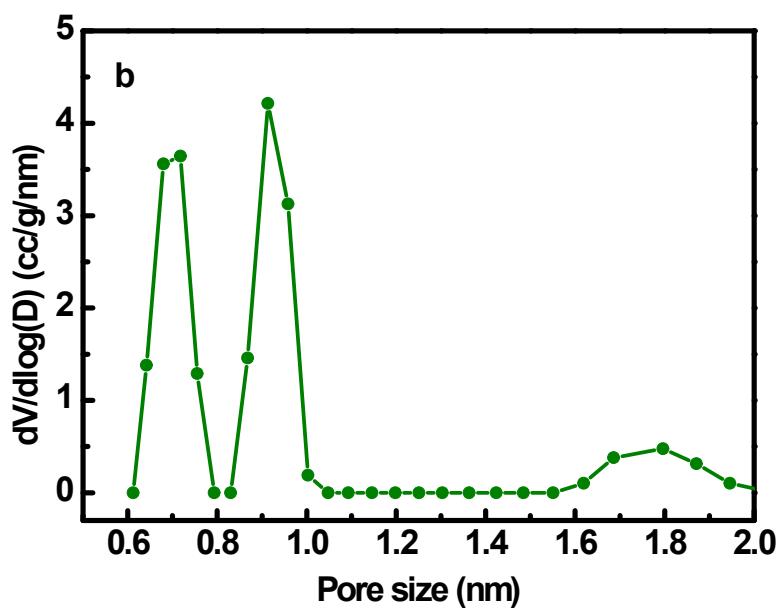


Fig. S5. Ar sorption isotherms (a) and pore size distribution (b) of fluorine-free UiO-66.