Supporting Information

An Efficient Modulated Synthesis of Zirconium Metal-Organic Framework UiO-66

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1. Synthesis

The amount of each reagent added to the 28 different syntheses is summarized in Table S1, where the quantities are provided in terms of their molar ratio with $ZrCl_4$ and by the actual mass or volume added. And the masses of products are also listed in Table S1.

Table S1 Molar ratio and masses or volume of the various reagents and mass of UiO-66 products.

Sample designation	Molar equivalents / Masses (g) or volume (mL)				Mass of products/g
	$ZrCl_4$/g	H_2BDC	DMF	Haloid acid	
UiO-66-free	1 / 0.9325	1 / 0.6602	64.6 / 20.0	0	0.29
UiO-66-1HBr	1 / 0.9325	1 / 0.6602	"	1 / 0.215	1.53
UiO-66-2 HBr	1 / 0.9325	1 / 0.6602	"	2 / 0.430	1.52
UiO-66-3 HBr	1 / 0.9325	1 / 0.6602	"	3 / 0.645	1.55
UiO-66-4 HBr	1 / 0.9229	1 / 0.6603	"	4 / 0.865	1.77
UiO-66-5 HBr	1 / 0.9229	1 / 0.6603	"	5 / 1.080	1.50
UiO-66-6 HBr	1 / 0.9229	1 / 0.6603	"	6 / 1.300	1.49
UiO-66-7 HBr	1 / 0.9229	1 / 0.6603	"	7 / 1.520	1.44
UiO-66-8 HBr	1 / 0.9229	1 / 0.6603	"	8 / 1.735	1.35
UiO-66-9 HBr	1 / 0.9229	1 / 0.6603	"	9 / 1.950	1.27
UiO-66-1HF	1 / 0.9328	1 / 0.6615	"	1 / 0.070	0.64
UiO-66-2 HF	1 / 0.9330	1 / 0.6614	"	2 / 0.140	0.63
UiO-66-3 HF	1 / 0.9330	1 / 0.6614	"	3 / 0.210	0.57
UiO-66-4 HF	1 / 0.9330	1 / 0.6640	"	4 / 0.275	0.55
UiO-66-5 HF	1 / 0.9330	1 / 0.6640	"	5 / 0.345	0.48

UiO-66-6 HF	1 / 0.9322	1 / 0.6630	“	6 / 0.415	0.30
UiO-66-7 HF	1 / 0.9322	1 / 0.6630	“	7 / 0.485	0.27
UiO-66-8 HF	1 / 0.9330	1 / 0.6619	“	8 / 0.555	0.22
UiO-66-9 HF	1 / 0.9330	1 / 0.6619	“	9 / 0.620	0.19
UiO-66-1HCl	1 / 0.9309	1 / 0.6622	“	1 / 0.125	1.17
UiO-66-2 HCl	1 / 0.9322	1 / 0.6629	“	2 / 0.245	1.37
UiO-66-3 HCl	1 / 0.9322	1 / 0.6629	“	3 / 0.370	1.30
UiO-66-4 HCl	1 / 0.9339	1 / 0.6628	“	4 / 0.495	1.44
UiO-66-5 HCl	1 / 0.9339	1 / 0.6628	“	5 / 0.615	1.39
UiO-66-6 HCl	1 / 0.9333	1 / 0.6623	“	6 / 0.740	1.37
UiO-66-7 HCl	1 / 0.9333	1 / 0.6623	“	7 / 0.865	1.46
UiO-66-8 HCl	1 / 0.9332	1 / 0.6629	“	8 / 0.985	1.42
UiO-66-9 HCl	1 / 0.9332	1 / 0.6629	“	9 / 1.110	1.38

2. Characterization

2.1. X-ray Diffraction Profiles Analysis

The crystalline structure of UiO-66 was analyzed by X-ray diffraction (XRD, D8-ADVANCED, Bruker) using Cu-Kα radiation in the range of 2θ = 3-50° at the step of 0.2° s^{-1}. The relatively intensity of the broad peak was calculated as the following Eq. and the relevant data were listed in Table S2. Table S3 showed the crystallite size derived from (111) reflection (FWHM the reflection) according to Schaler's formula.

$$Rel(I)_{BP} = \frac{I_{BP}}{\frac{I(111) + I(200) + I(600)}{3}} \times 100$$

Table S2 Intensity of three most intense reflections and relatively intensity of the broad peaks of UiO-66 samples obtained with different amounts of haloid acid additive.

Sample designation	Intensity of the most intense reflections[a]				
	2-7°	(111)7.3°	(200)8.5°	25.8°	$Rel(I)_{BP}$, %
UiO-66-free					
UiO-66-1HBr	1318	8054	2565	3347	28.31
UiO-66-2 HBr	1197	7937	2058	2733	28.21
UiO-66-3 HBr	1804	8462	1852	2403	42.56
UiO-66-4 HBr	1597	10829	2105	1082	34.18
UiO-66-5 HBr	18	4342	939	270	0.97
UiO-66-6 HBr	1203	8333	1513	1011	33.24

UiO-66-7 HBr	1476	6450	994	1144	51.56
UiO-66-8 HBr	1257	11729	1881	1339	25.23
UiO-66-9 HBr	1366	6474	1235	1788	43.15
UiO-66-2 HF	951	13941	2893	883	16.10
UiO-66-2 HCl	1353	4130	897	390	74.93

[a] Expressed by peak area.

Schaler's formula:

$$D = \frac{0.89\lambda}{\beta\cos\theta} = \frac{0.89 \times 0.154056}{\frac{FWHM}{180} \times 3.14 \times \cos\frac{2\theta}{2}}$$

Table S3 Crystallite size of UiO-66 samples synthesized with different amount of modulator.

Sample designation	2θ	FWHM (111)	D/nm	λ
UiO-66-free				
UiO-66-1HBr	7.360	0.198	39.8	
UiO-66-2 HBr	7.379	0.252	31.3	
UiO-66-3 HBr	7.400	0.287	27.4	
UiO-66-4 HBr	7.422	0.270	29.2	
UiO-66-5 HBr	7.359	0.235	33.5	
UiO-66-6 HBr	7.420	0.257	30.6	0.154056
UiO-66-7 HBr	7.419	0.274	28.7	
UiO-66-8 HBr	7.420	0.282	27.9	
UiO-66-9 HBr	7.480	0.243	32.4	
UiO-66-2 HF	7.418	0.238	33.1	
UiO-66-2 HCl	7.441	0.325	24.2	

2.2. TGA Calculations

Table S4 Missing-linker deficiency of obtained samples synthesized with haloid acid additive.

Sample designation	TGA		BDC	Missing linkers, %
	Theoretical value, %	Experimental value, %		
UiO-66-free		195.78	4.8	20.32
UiO-66-1HBr		188.02	4.4	26.78
UiO-66-2HBr		197.95	4.9	18.51
UiO-66-3HBr	220.25	196.26	4.8	19.91
UiO-66-4HBr		195.22	4.8	20.78
UiO-66-5HBr		191.5	4.6	23.88
UiO-66-6HBr		191.82	4.6	23.61

UiO-66-7HBr	191.83	4.6	23.61
UiO-66-8HBr	190.94	4.5	24.34
UiO-66-9HBr	187.45	4.4	27.25
UiO-66-2HF	206.17	5.3	11.67
UiO-66-2HCl	192.00	4.6	23.46

2.3. Nitrogen Adsorption

N_2 adsorption and desorption isotherms of UiO-66 were recorded at 77 K using an ASAP 2460 analyzer (Micromeritics). 200–250 mg of one sample was outgassed at 120 ºC for 12 h in vacuo prior to the measurement. The total surface area and the mesoporous surface area were respectively calculated from the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods. The microporous surface area was obtained by subtracting the mesoporous surface from the total surface area. The micropore size distribution was calculated using the NLDFT method.

Table S5 Some properties of obtained samples.

Sample designation	SSA(BET), m^2/g	Microporous area, m^2/g	Micropore volume, cm^3/g	Total pore volume, cm^3/g
UiO-66-free	325	331	0.132	0.377
UiO-66-1HBr	1527	1397	0537	0.632
UiO-66-2HBr	1451	1273	0.516	0.639
UiO-66-3HBr	1401	1184	0.512	0.672
UiO-66-4HBr	1411	1227	0.453	0.580
UiO-66-5HBr	1309	1127	0.427	0.553
UiO-66-6HBr	1249	1065	0.412	0.540
UiO-66-7HBr	1216	1030	0.393	0.538
UiO-66-8HBr	1088	887	0.384	0.543
UiO-66-9HBr	1134	935	0.371	0.535
UiO-66-2HF	1442	1355	0.501	0.561
UiO-66-2HCl	1630	1486	0.532	0.636