Electronic Supplementary Information

for

Water as a structure-driving agent between UiO-66 and MIL-140A metal-organic frameworks

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1. Synthesis parameters for UiO-66 and MIL-140A from literature data

Table S 1 Synthesis parameters of Zr-BDC MOFs from selected literature.

№	Molar ratio Zr^{4+}:BDC^{2-}	Mol of solvent	Modulator	Temperature, °C	Duration	SSA (BET)[a], m^2/g	N_2 capacity [b], cm^3/g	ref.
1	1:1.4	358.8 DMF	0.06 HCl	80	12 h	1580	410	1
2	1:1	100 DMF, 3H_2O	0.79 HCl, 29.6 BA	110	48 h	N/R	N/R	2
3[c]	1:1	115 DMF	100 FA	120	24 h	1367	350	3
4	1:1	150.4 DMF, 1.33 H_2O	50.3 AA	100	14 days	1530	400	4
5	1:1, 4:5, 2:3, 4:7, 1:2	77.5 DMF	2 HCl	100, 160, 220	20 h	1105-1455	280-390	5
6	1:1	750 DMF, 4H_2O	0, 1, 3, 5, 10, 20, 30 BA	120	24 h	700-1400	N/R	6
7	1:1	133 DMF	1.13 HCl, 10,20 CFCOOH	120	21 h	N/R	N/R	7
8[d]	1:1	178.6 DMF	- / 0.176 NH_4OH	120	24 h	1433/ 1320	370-390	8
9[e]	1:2	77.5 DMF	2 HCl	220	16 h	1067	300	9
10	1:1.12	800 DMF	135AA	120	24 h	1194[L]	400	10
11[f]	1:1	115 DMF	100 FA	120	5 min	1087	250	3
12	1:1	103.3DMF, 6H_2O	30 AA	120 (90-120)	15 min (10-20 min)	982-1206	300-400	11
13	1:1.12	800 DMF	-/135AA/30BA	100	2 h	888-1661[L]	200-350	10
14	1:2	81 DMF	-	220	16 h	415	110	12
15	1:1	129 DMF	7 AA	220	20 min	335	N/R	13
16[g]	1:1	77.5 DMF	3.5 AA	220	30 min	396	N/R	14

N/R = not reported

[a] calculated SSA values for UiO-66=1125 [5] , MIL-140A = 360 m^2/g [12].

[b] for relative pressure P/P_0 = 0.9 at 77 K.

[c] H_2 capacity – 1.5 wt. % at 77 K and approximately 1 bar.

[d] CO_2 capacity - 8.1 mmol/g at 273 K, 988 kPa.

[e] CO_2 capacity - 5.5 mmol/g at 303 K, 988 kPa.

[f] H_2 capacity – 1.26 wt. % at 77 K and approximately 1 bar.

[g] CO_2 capacity – 0.9 mmol/g at 293 K, 120 kPa.

[L] specific surface area was calculated according to Langmuir model

2. Synthesis details

Starting materials. Zirconium tetrachloride $ZrCl_4$, H_2BDC, DMF and M-ZrO_2 NPs – all were of analytical grade and were used as received from commercial suppliers. T-ZrO_2 NPs were obtained from thermal decomposition of UiO-66 at 700 °C for 3 h in air. XRPD, and FTIR proved the total combustion of the starting material. Deionized (DI) water (18 MΩ·cm) was obtained from Milli-Q ultra-pure water system.

In a typical synthesis, $ZrCl_4$ was dissolved in DMF, and H_2BDC was added under stirring. Into the samples 1:1:3_120-UiO, 1:2:3_120-UiO, 1:1:3_220-UiO and 1:2:3_220-UiO we added water. For synthesis at 120 °C solution in the glass flask was placed into the preheated oven for 24 h. For synthesizes at 220 °C we used hermetically closed steel autoclaves with Teflon inner vessels. The precipitate was collected by centrifuging, then washed twice with DMF and ones with methanol, and dried at 150°C in the air.

3. XRPD

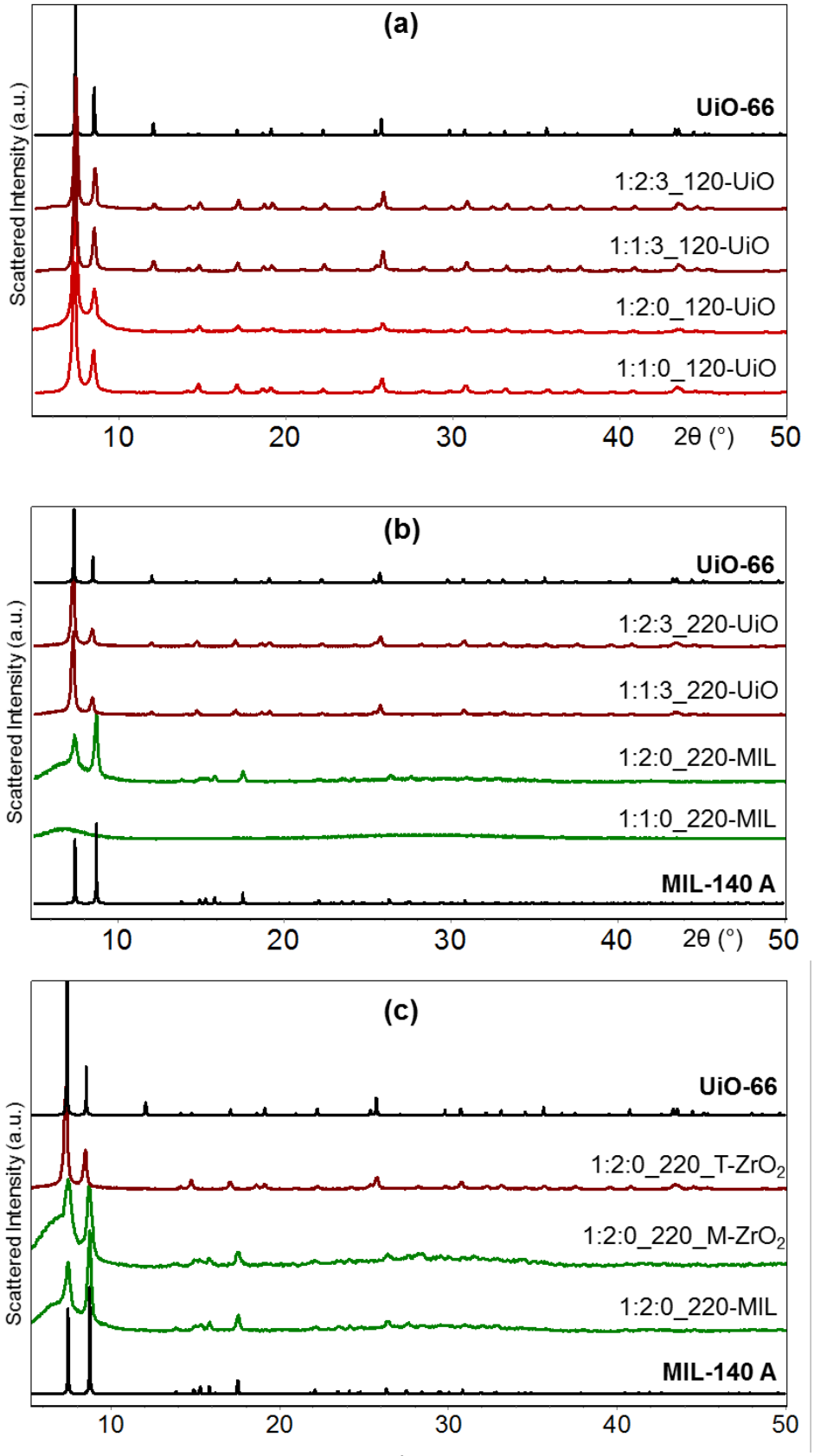

Fig. S 1 Full range XRPD profiles (λ = 1.5406 Å) measured for samples synthesized at 120 °C (a) and at 220 °C (b). The patterns labelled as UiO-66 and MIL-140A are calculated from the literature cif data for UiO-66[2] and MIL-140A.[12]

4. Characterization of the samples

4.1.TGA

Temperature of decomposition occurs, according to TGA, in the 540-545 °C (in nitrogen) and 510-520 °C (in air) intervals for both samples (Fig. S 2). Experimental weight loss for 1:2:3-220-UiO sample with UiO-66 structure is 43% and for 1:2:0-220-MIL sample with MIL-140A structure is 55% in good agreement with theoretical values – 48.5 % for UiO-66 and 54.6 % for MIL-140A.

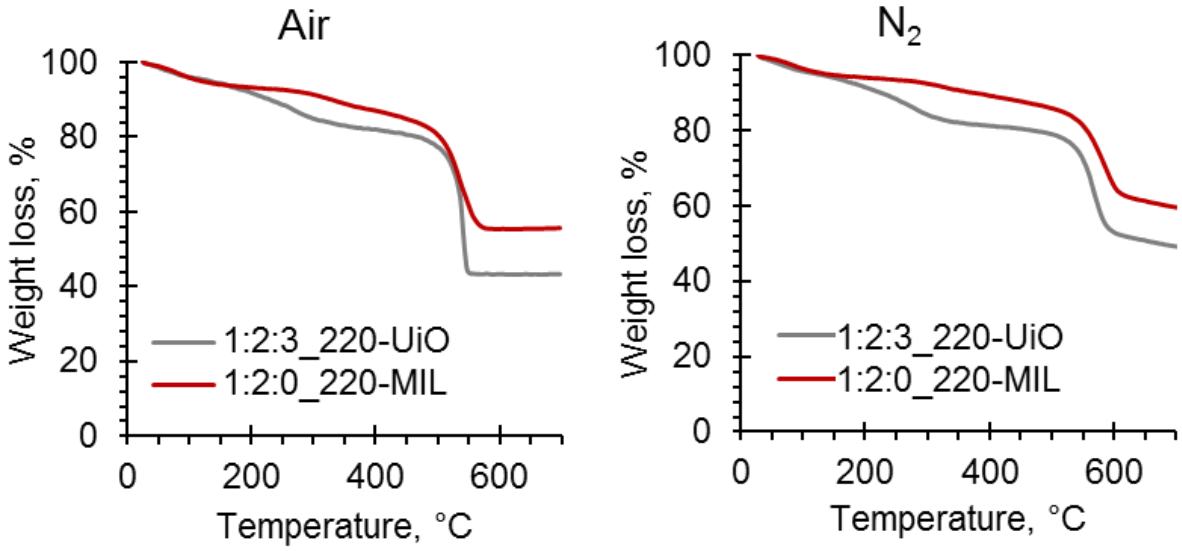

Fig. S 2 TGA measured in airflow (left) and in N_2 (right) of the samples 1:2:3_220-UiO and 1:2:0_220-MIL.

4.2. Nitrogen adsorption

The N_2 adsorption isotherms are reported in Fig. S2a and S2b for samples synthesized at 120 and 220 °C, respectively. Quantitative results are summarized in Table S2.

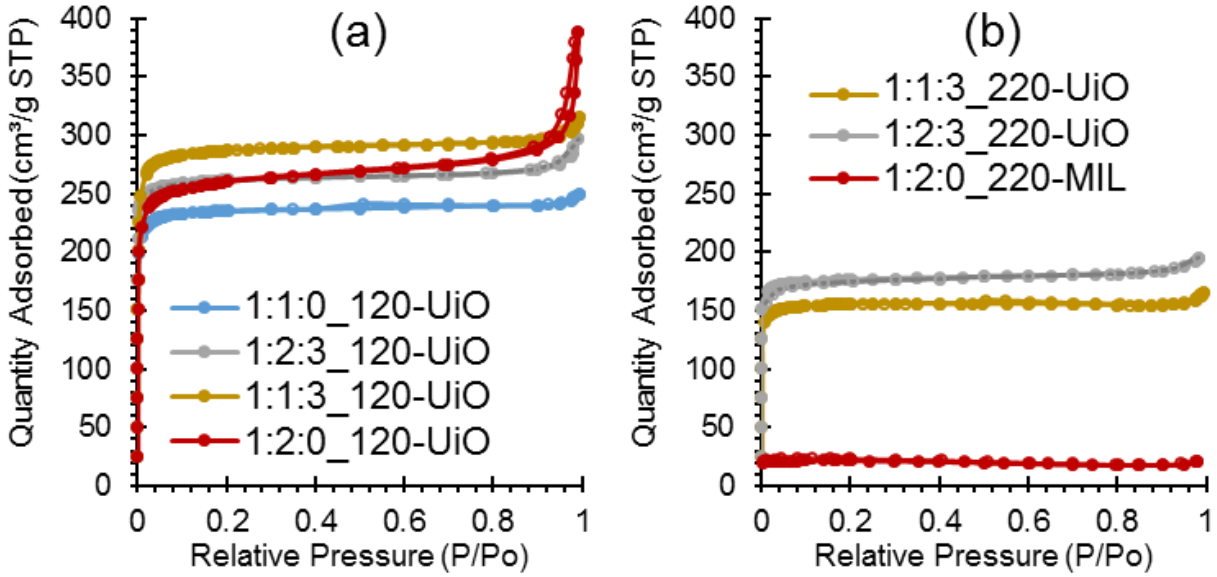

Fig. S 3 Nitrogen adsorption-desorption isotherms of samples obtained at 120 °C (a) and 220 °C (b). Filled markers corresponds to adsorption branch of isotherm and open one for desorption branch.

Table S 2 Specific surface areas and pore volumes of synthesized samples

Sample designation	SSA[i], m^2/g		Pore volume[ii], cm^3/g
	BET	Langmuir	
1:1:3-120-UiO	1155	1243	0.41
1:1:0-120-UiO	954	1014	0.38
1:2:3-120-UiO	1058	1130	0.44
1:2:0-120-UiO	1017	1119	0.49
1:1:3-220-UiO	630	669	0.22
1:2:3-220-UiO	718	751	0.26
1:2:0-220-MIL	89	94	0.03

[i] Specific surface area

[ii] Pore volumes were calculated at $P/P_0=0.97$

1:1:0-220-MIL was characterized as amorphous, so its SSA was not measured. Low SSA value of the sample 1:2:0-220-MIL (compared with theoretical SSA of MIL-140A 360 m^2/g) could be attributed to the presence of amorphous phase according to XRPD.

5. Thermal decomposition of UiO-66

XRPD and TEM characterization of the T-ZrO_2 NPs obtained after full thermal decomposition at 700 °C of the UiO-66 sample in the air for 3 h.

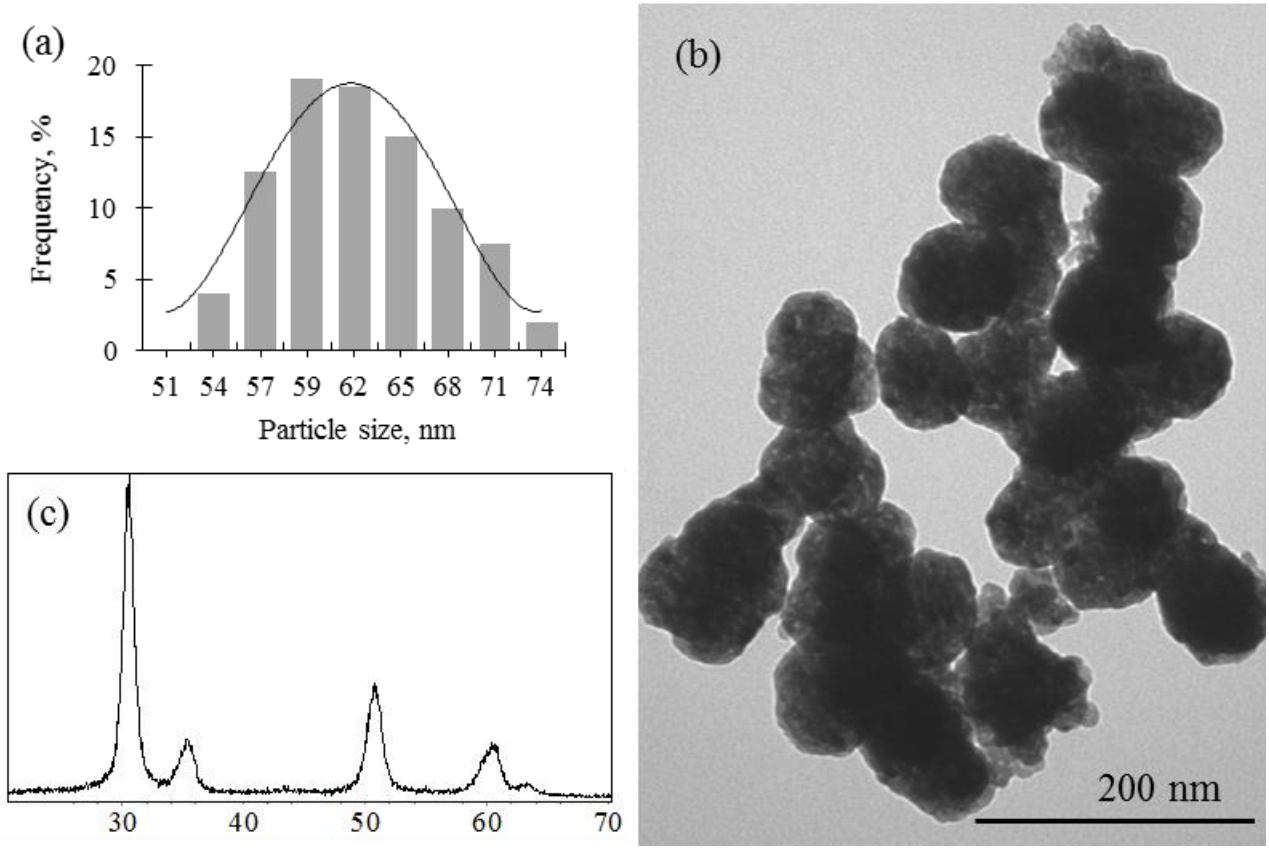

Fig. S 4 Powder of T-ZrO_2, obtained after full thermal decomposition of the UiO-66 sample at 700 °C in the air for 3 h. (a) Particle size distribution from the TEM data. (b) Representative TEM image. (c) XRPD profile of the sample.

6. FTIR spectra

Fig. S5a,b reports a magnification of the FTIR spectra reported in the main Fig. 1b,d of the main text.

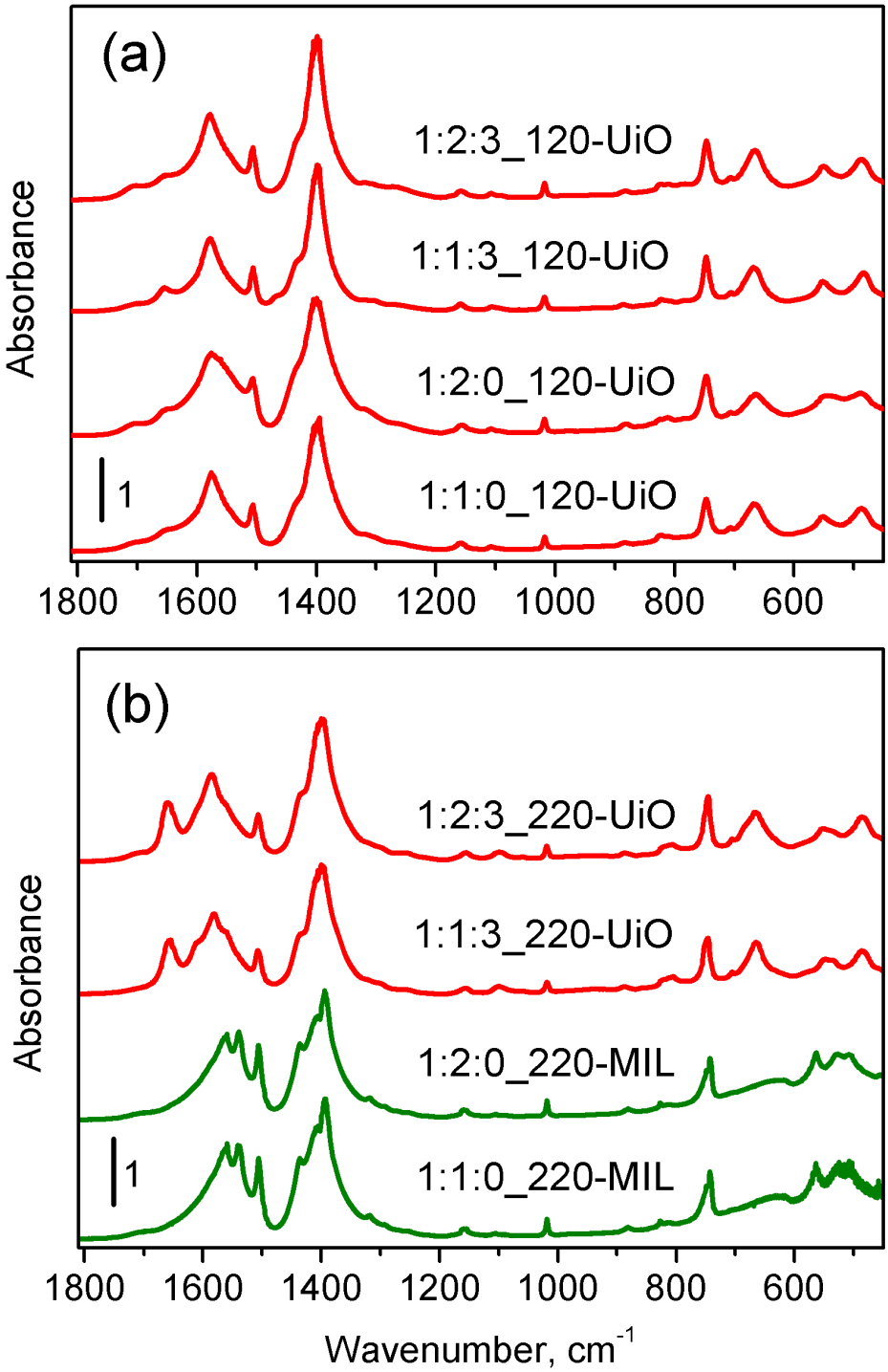

Fig. S 5 FTIR spectra of desolvated samples synthesized at 120 °C (a) and 220 °C (b). Patterns and spectra have been vertically translated for clarity.

7. Summarizing scheme

Fig. S6 summarized the main message of the present study.

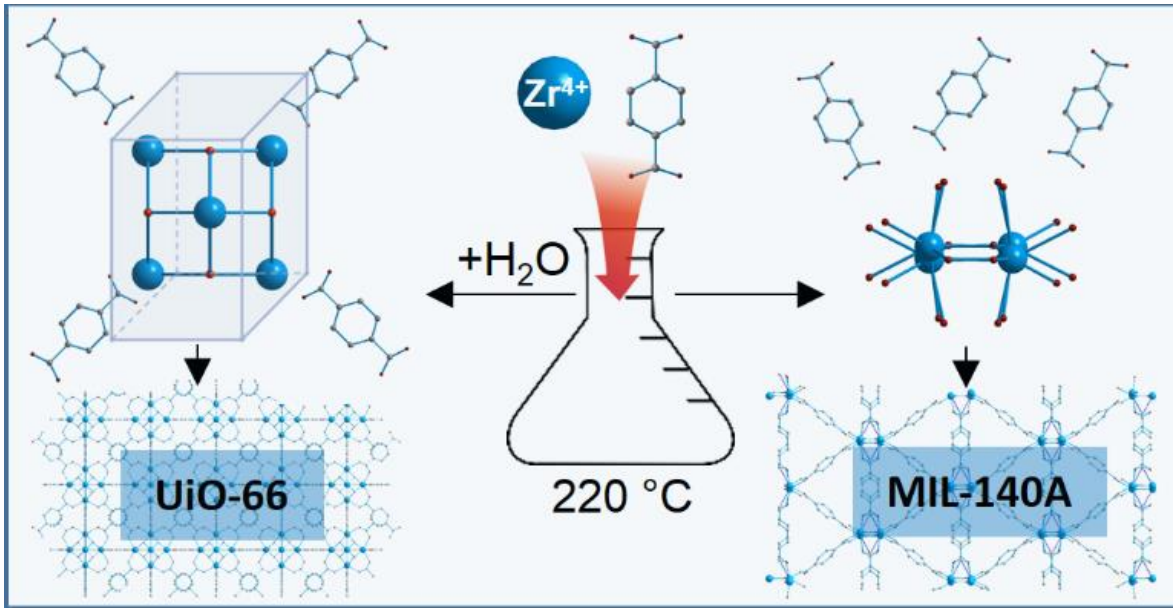

Fig. S 6 Schematic picture describing the outcome of the synthesis at 220 °C. The Presence of water drives the synthesis towards the UiO-66 phase (left);

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