

Electronic Supplementary Information for Dalton Transactions  
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### **Supporting Information For**

#### **Enhanced Selectivity of CO<sub>2</sub> over CH<sub>4</sub> in Sulphonate-, Carboxylate- and Iodo-Functionalized UiO-66 Frameworks**

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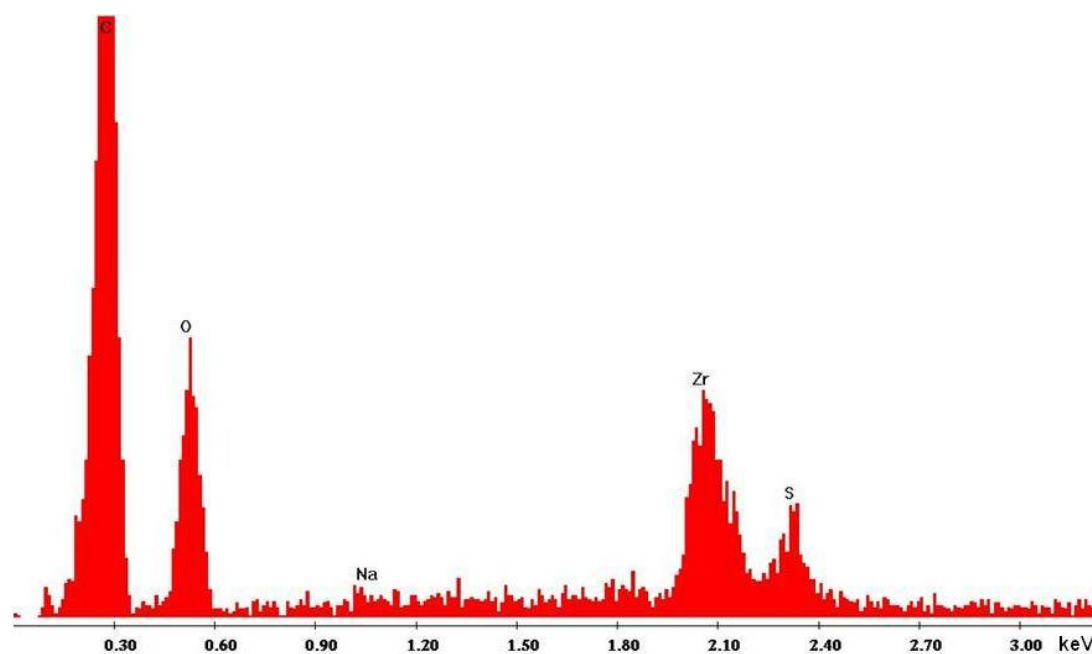
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### Elaboration of the strategy used for the synthesis of the UiO-66-X compounds:

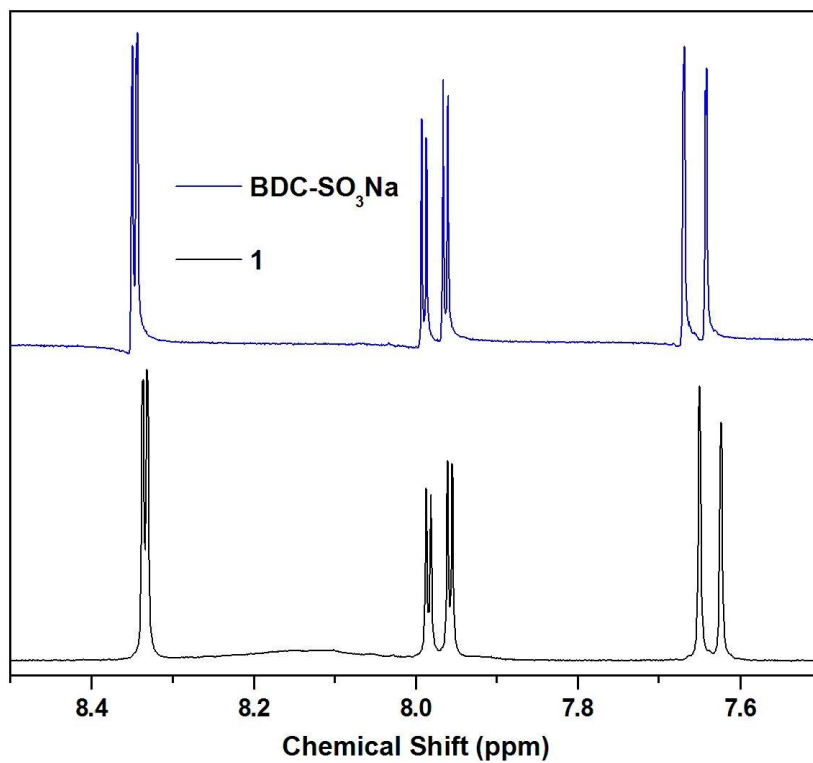
High-throughput methods were used in order to achieve the optimum reaction conditions for syntheses of the three UiO-66-X compounds. In short, for a particular Zr salt and a particular H<sub>2</sub>BDC-X linker in a particular solvent, 6 different additives/modulators (H<sub>2</sub>O, conc. HCl, benzoic acid, formic acid, acetic acid or trifluoroacetic acid) can be added resulting in 6 different reaction mixtures. Thus, for the synthesis of a particular UiO-66-X compound at a particular temperature, 18 (= 3 × 6) different reaction mixtures can be prepared in 3 different solvents (*N,N'*-dimethylformamide, *N,N'*-diethylformamide and *N,N'*-dimethylacetamide). For three Zr salts (ZrCl<sub>4</sub>, ZrOCl<sub>2</sub>·8H<sub>2</sub>O and ZrO(NO<sub>3</sub>)<sub>2</sub>·xH<sub>2</sub>O), a total of 54 (= 3 × 18) combination of reactants are possible. These reaction mixtures were heated at a particular temperature in a heating block that can concomitantly heat 24 glass tubes containing the reaction mixtures.

The 18 possible combinations of reactants for the synthesis of compound **1** using ZrOCl<sub>2</sub>·8H<sub>2</sub>O and BDC-SO<sub>3</sub>Na at 150 °C.

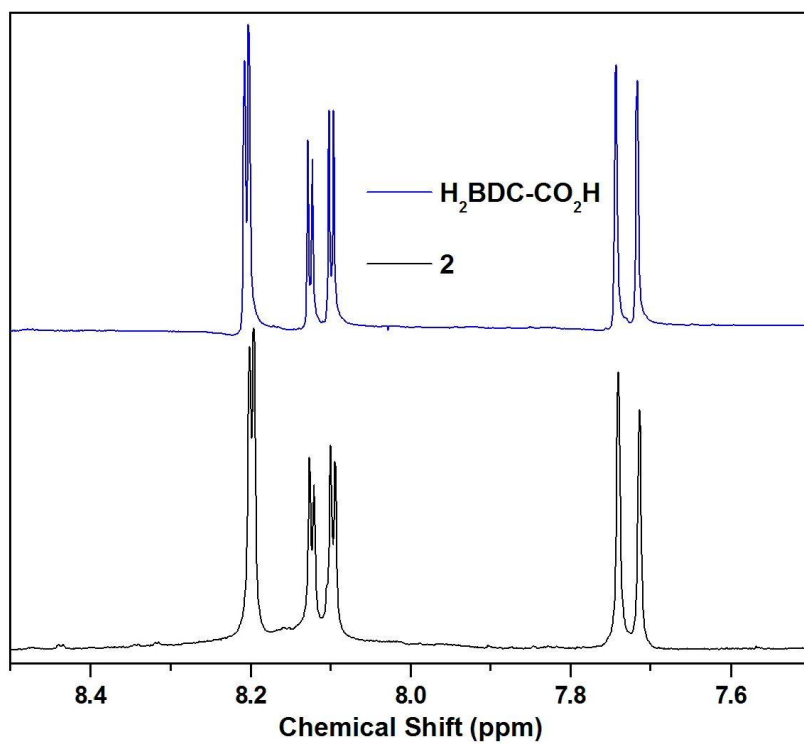
solvent \ additive	water	conc. HCl	benzoic acid	formic acid	acetic acid	trifluoroacetic acid
<i>N,N'</i> -dimethylformamide	○	○	○	○	○	○
<i>N,N'</i> -diethylformamide	○	○	○	○	○	○
<i>N,N'</i> -dimethylacetamide	○	○	○	○	○	○



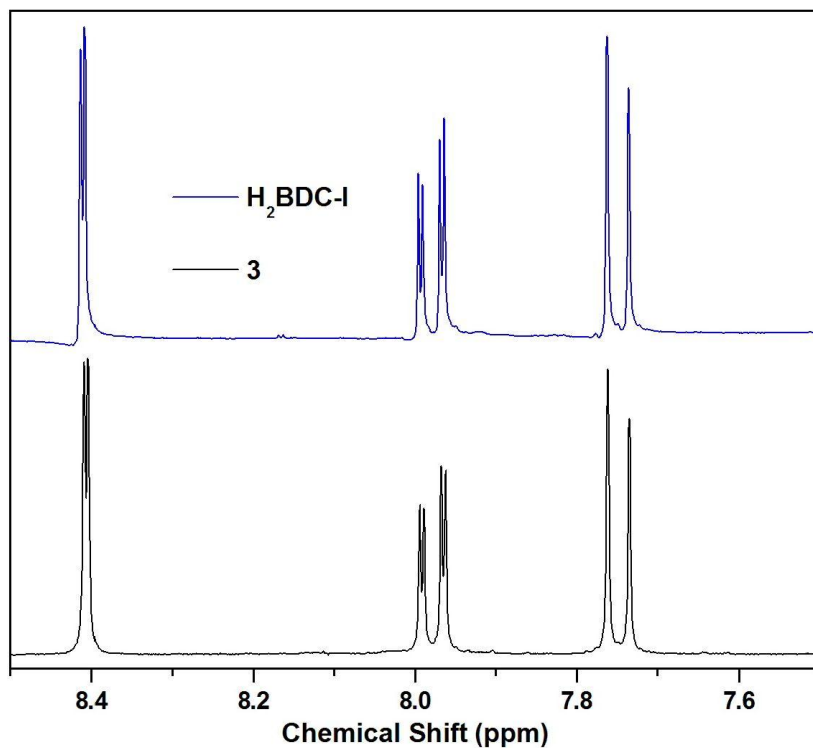
**Figure S1.** EDX spectrum of compound **1** recorded with an accelerating voltage of 20 kV. The expected peak position of sodium atom in the EDX spectrum has been high-lighted, although no sodium has been detected.



**Figure S2.** <sup>1</sup>H-NMR spectra of compound **1** (black) and BDC-SO<sub>3</sub>Na linker (blue) recorded in 570 μL of d<sub>6</sub>-DMSO and 30 μL of 48% HF.



**Figure S3.**  $^1\text{H-NMR}$  spectra of compound **2** (black) and BDC- $\text{CO}_2\text{H}$  linker (blue) recorded in 570  $\mu\text{L}$  of  $\text{d}_6\text{-DMSO}$  and 30  $\mu\text{L}$  of 48% HF.



**Figure S4.**  $^1\text{H-NMR}$  spectra of compound **3** (black) and BDC-I linker (blue) recorded in 570  $\mu\text{L}$  of  $\text{d}_6\text{-DMSO}$  and 30  $\mu\text{L}$  of 48% HF.

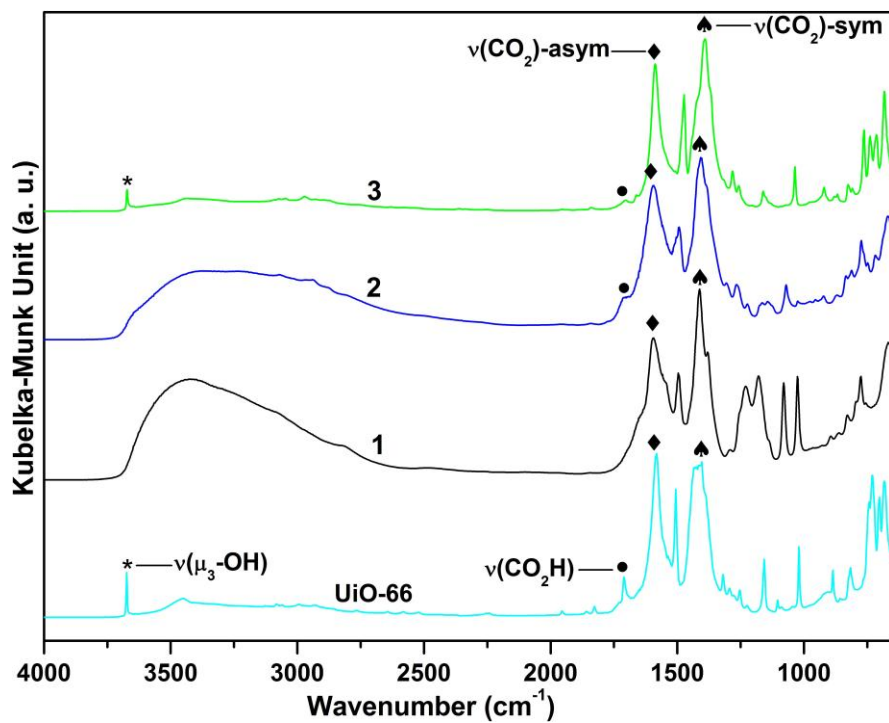


Figure S5. DRIFT spectra of the as-synthesized UiO-66-X compounds.

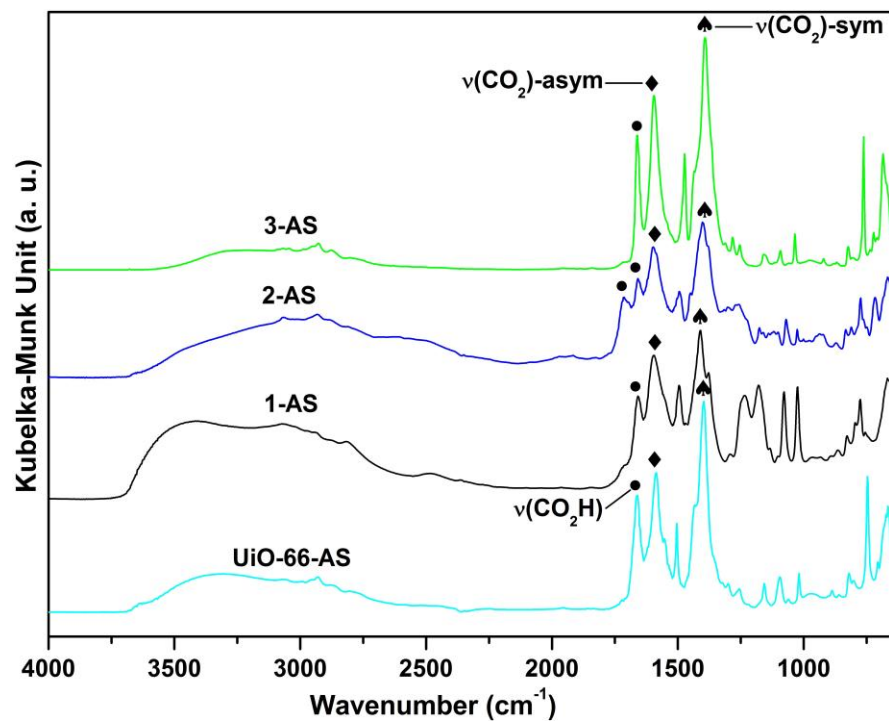
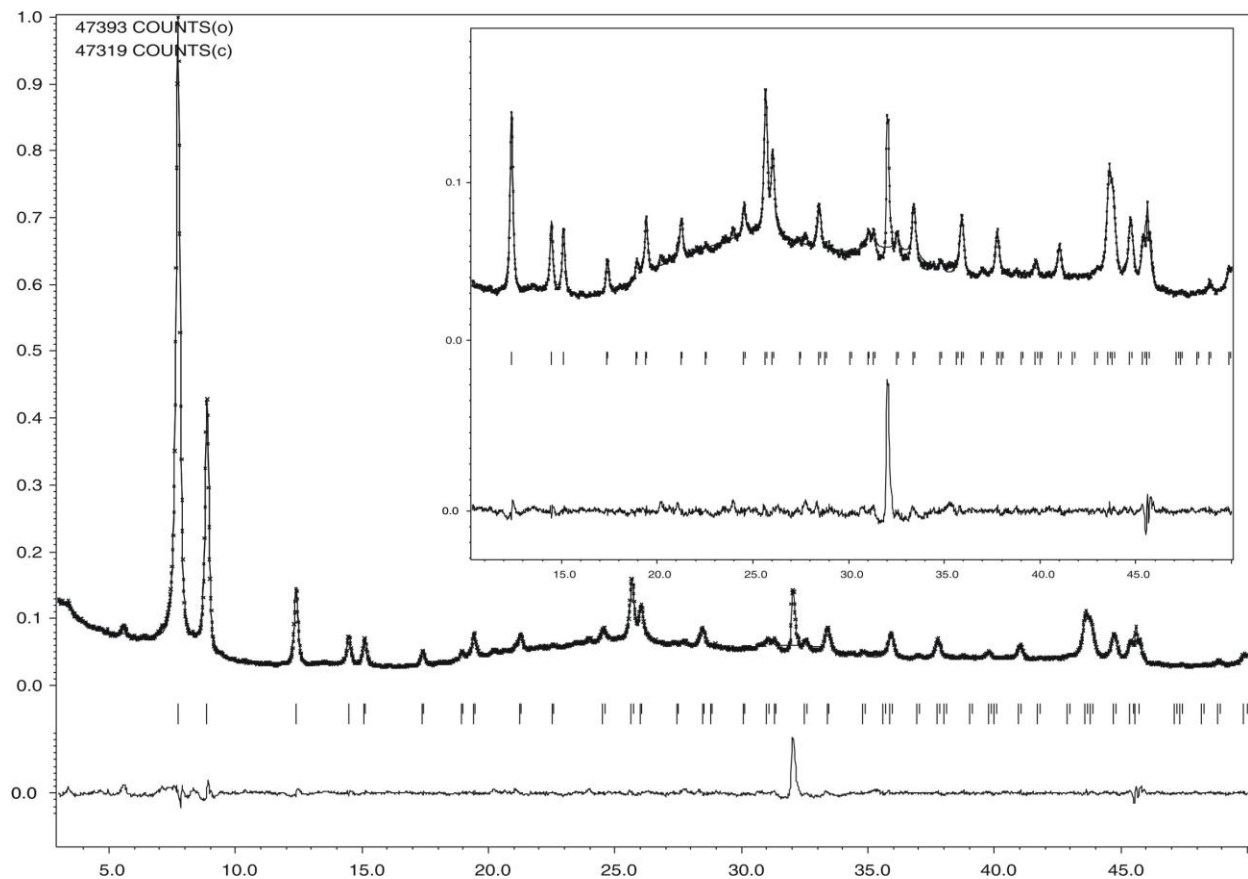
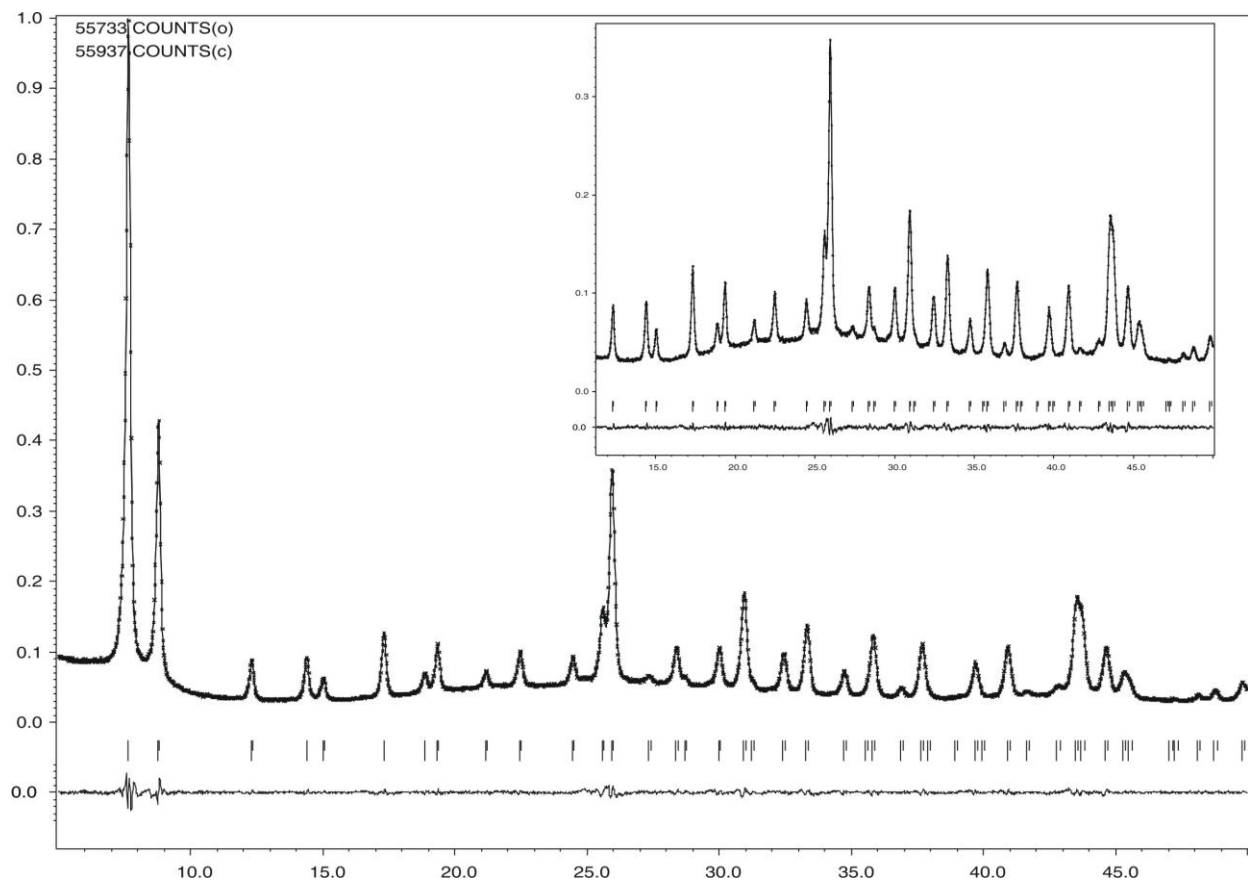


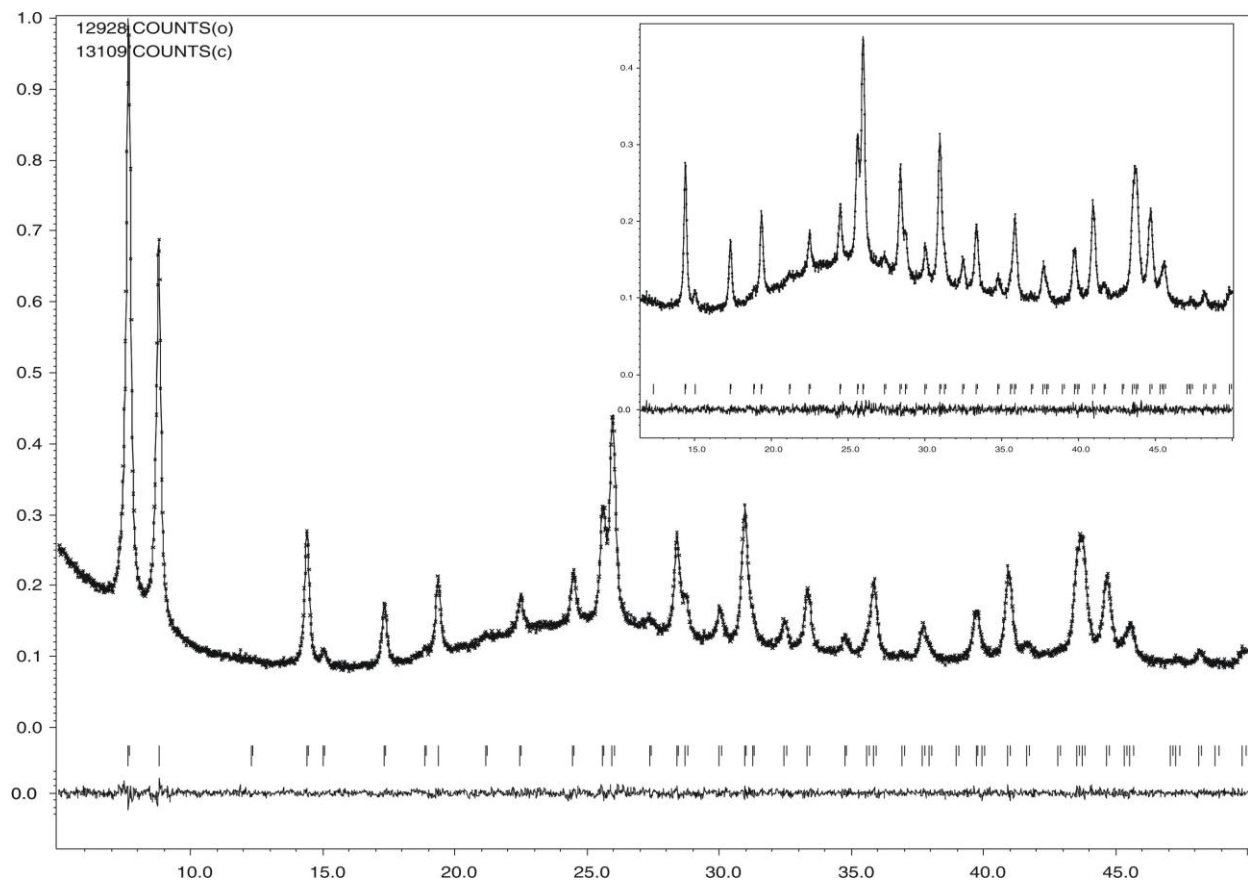
Figure S6. DRIFT spectra of the hydrated UiO-66-X compounds.



**Figure S7.** Le Bail fit of the XRPD pattern of compound **1**. Dotted and solid lines represent observed and calculated patterns, respectively with peak markers and the difference plot shown at the bottom. The peak at 32.04°  $2\theta$  corresponds to the sample holder.  $R_p = 3.58$ ,  $R_{wp} = 6.56$ ,  $\chi^2 = 3.54$ .

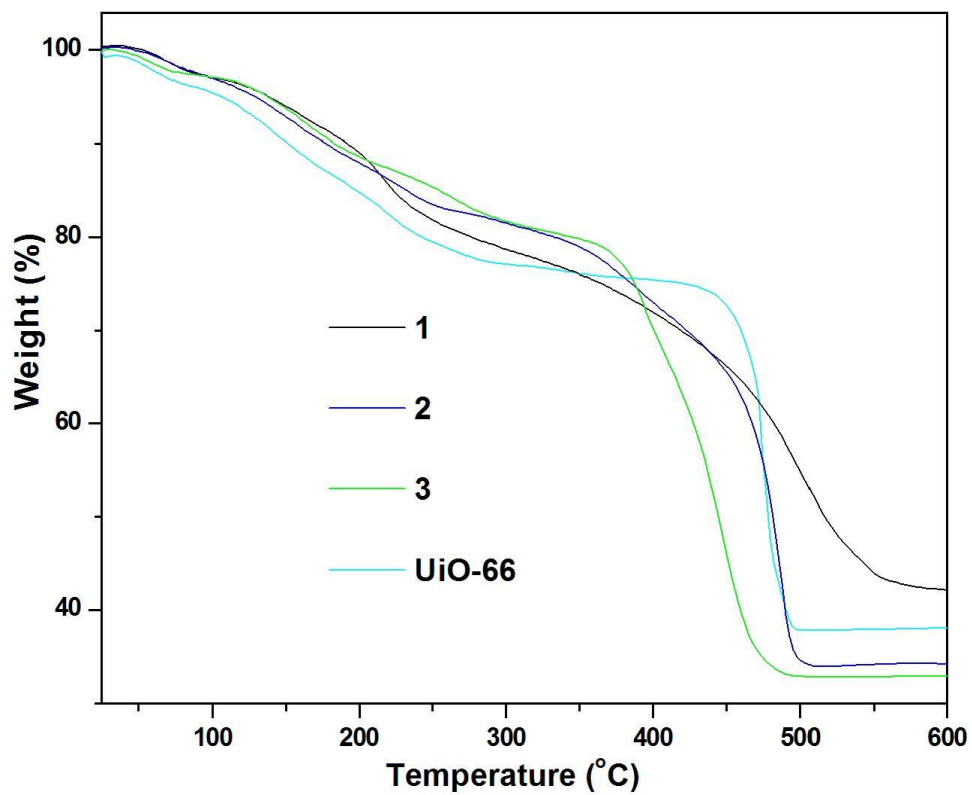


**Figure S8.** Le Bail fit of the XRPD pattern of compound **2**. Dotted and solid lines represent observed and calculated patterns, respectively with peak markers and the difference plot shown at the bottom.  $R_p = 2.21$ ,  $R_{wp} = 2.77$ ,  $\chi^2 = 1.68$ .

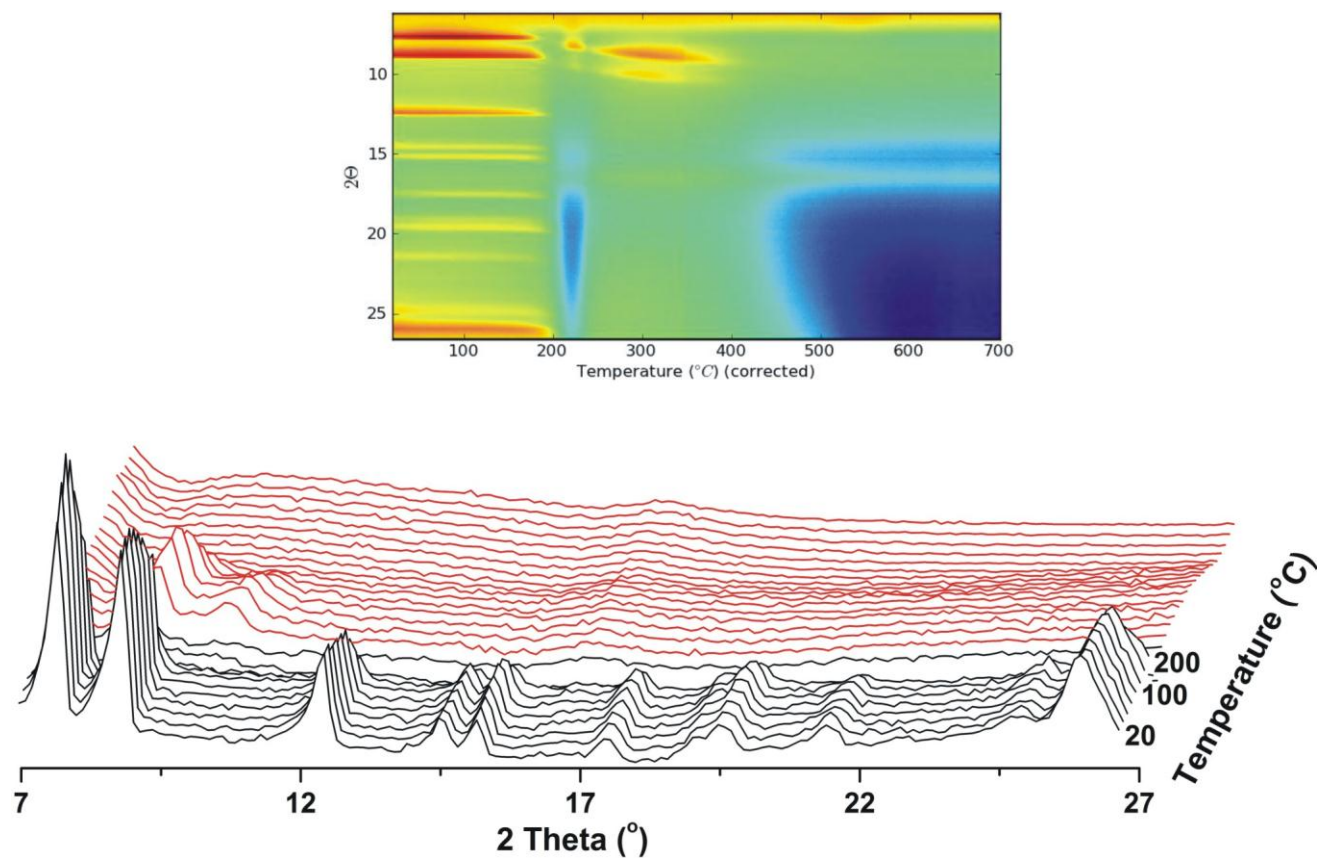


**Figure S9.** Le Bail fit of the XRPD pattern of compound **3**. Dotted and solid lines represent observed and calculated patterns, respectively with peak markers and the difference plot shown at the bottom.  $R_p = 2.00$ ,  $R_{wp} = 2.55$ ,  $\chi^2 = 1.11$ .

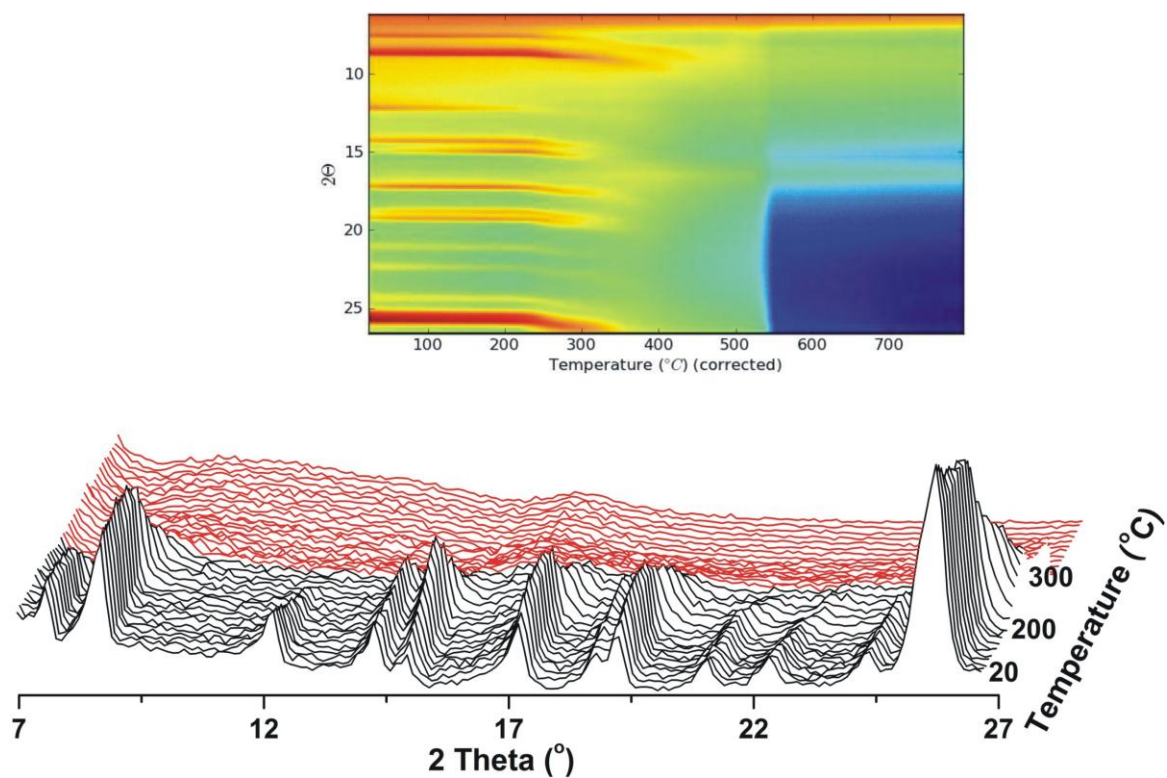




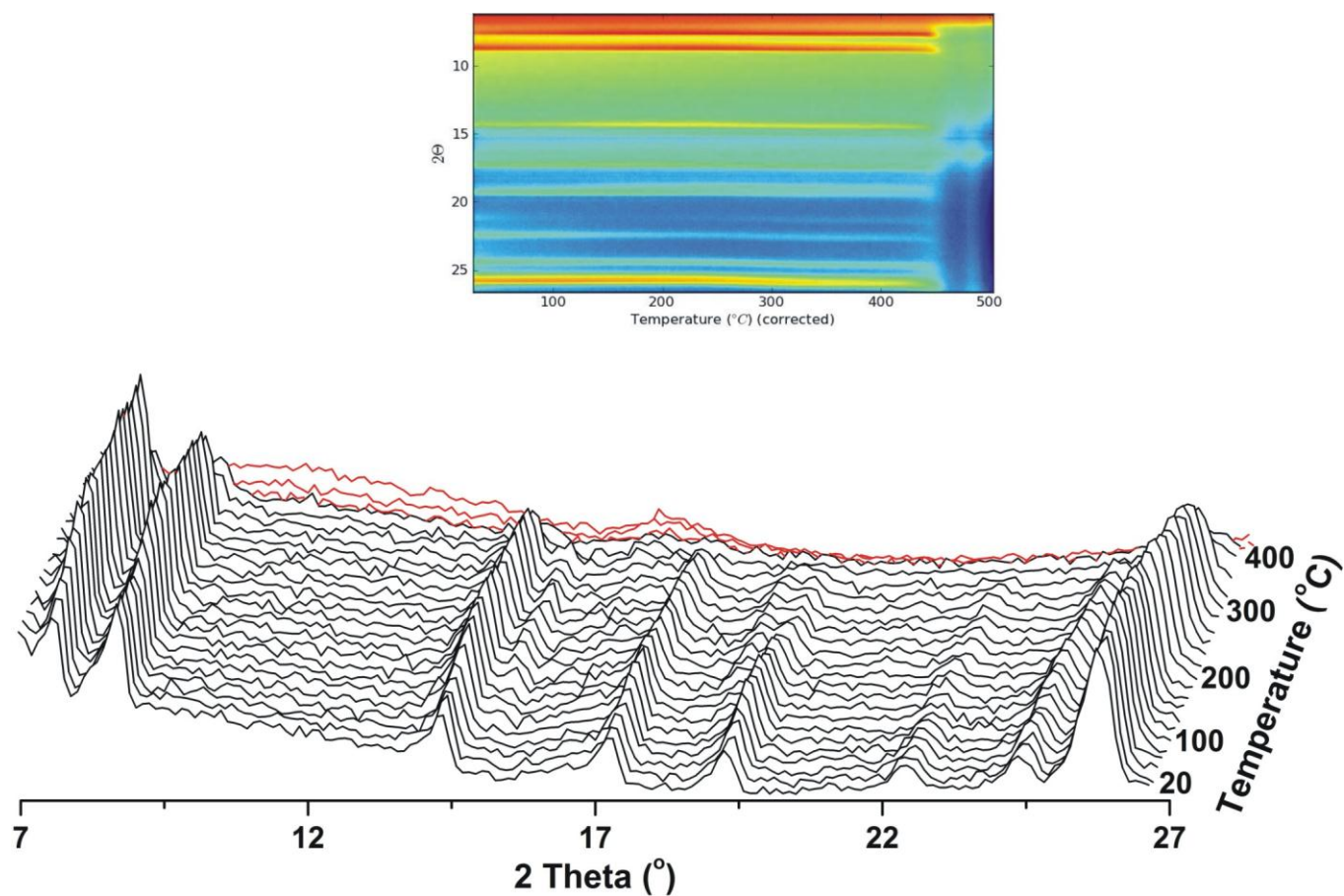
**Figure S10.** TG curves of as-synthesized **1** (black), **2** (blue), **3** (red) and UiO-66 (cyan) recorded in air atmosphere.



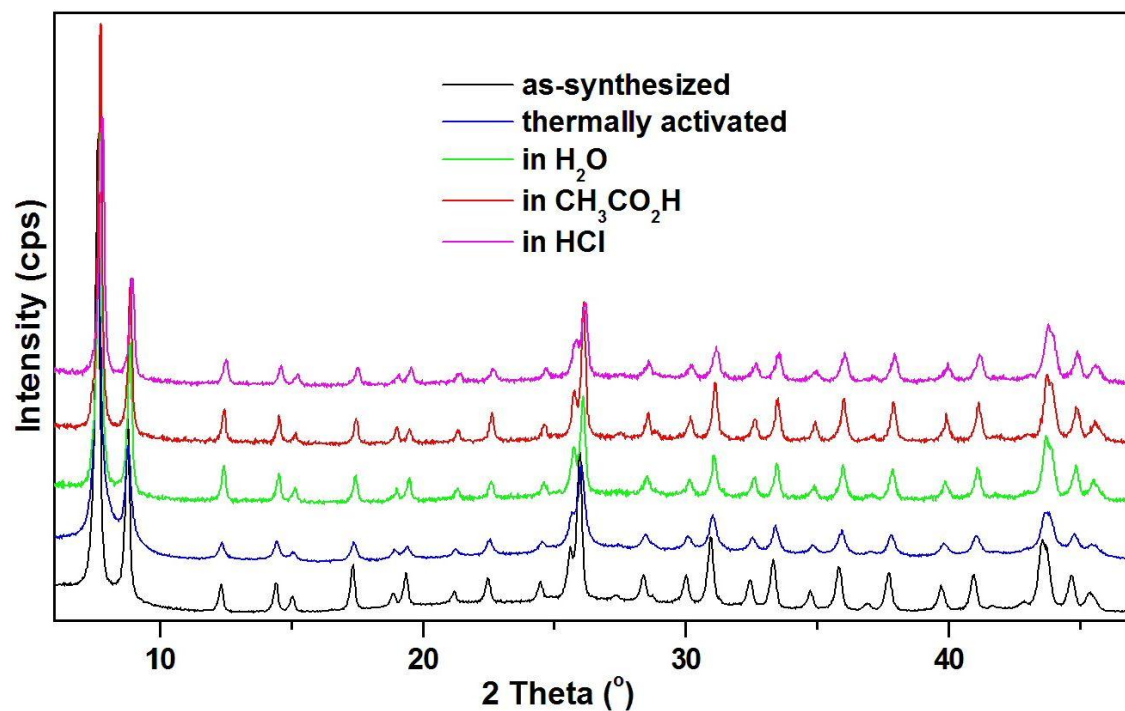
**Figure S11.** TDXRPD patterns of **1-AS** measured in air atmosphere in the range of 20-700 °C. The black and red patterns denote stable and decomposed phases, respectively. The variation of the intensities of the Bragg peaks as a function of temperature is shown on the top.



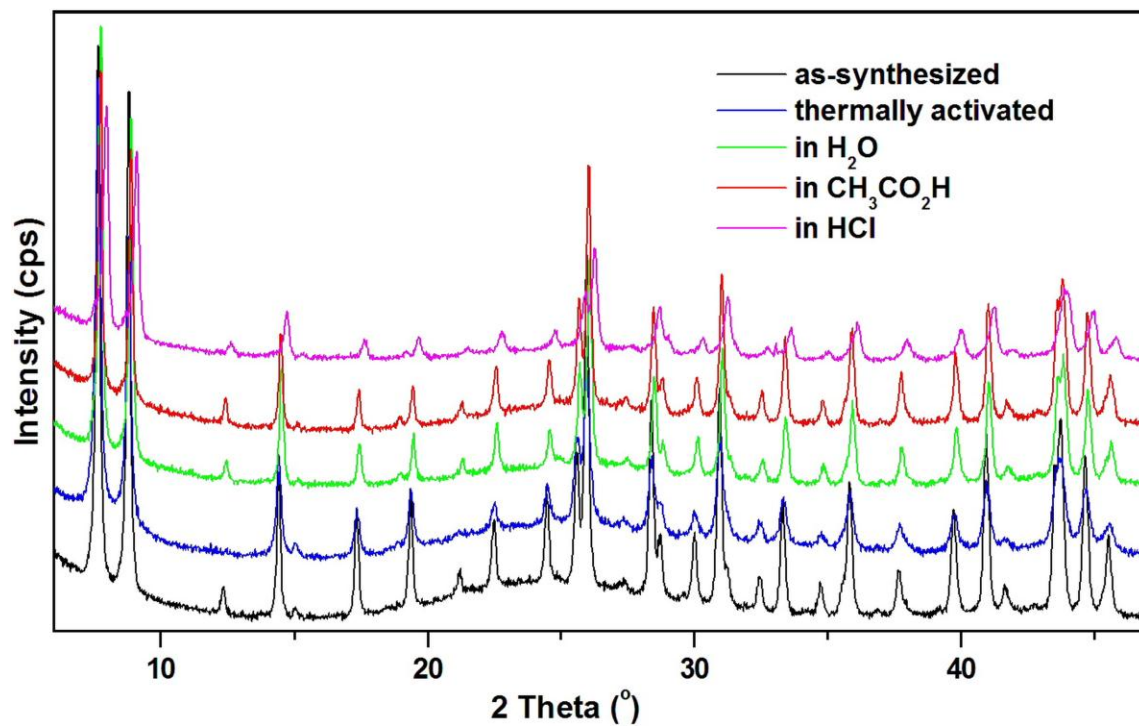
**Figure S12.** TDXRPD patterns of **2-AS** measured in air atmosphere in the range of 20-800 °C. The black and red patterns denote stable and decomposed phases, respectively. The variation of the intensities of the Bragg peaks as a function of temperature is shown on the top.



**Figure S13.** TDXRPD patterns of **3-AS** measured in air atmosphere in the range of 20-500 °C. The black and red patterns denote stable and decomposed phases, respectively. The variation of the intensities of the Bragg peaks as a function of temperature is shown on the top.

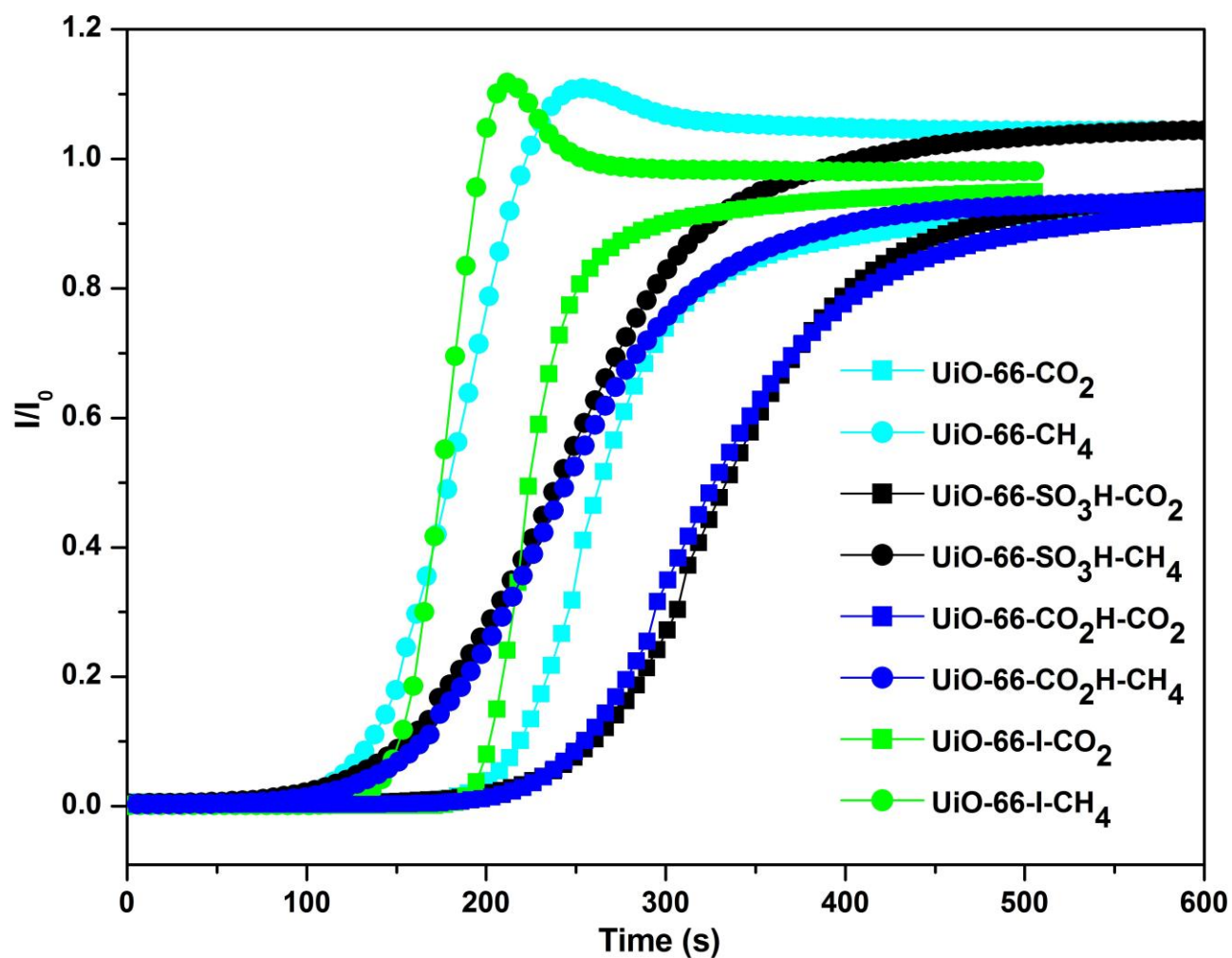


**Figure S14.** XRPD patterns of **2** in different forms: as-synthesized (black), thermally activated (blue), treated with water (green), acetic acid (red) and 1M HCl (magenta).



**Figure S15.** XRPD patterns of **3** in different forms: as-synthesized (black), thermally activated (blue), treated with water (green), acetic acid (red) and 1M HCl (magenta).

**Methods for breakthrough experiments:** The CO<sub>2</sub>-CH<sub>4</sub> breakthrough experiments were performed using a column with a length of 37 cm and an internal diameter of 0.4 cm, which was packed with 500 mg of MOF pellets, which were prepared by pressing the MOF powder samples under 2 MPa for one minute. Before each experiment, the adsorbent was regenerated by flowing pure He through the column for 30 min. The separation experiments were carried out at 298 K and under total flow of 40 mL/min (CO<sub>2</sub>: 20 mL/min, CH<sub>4</sub>: 20 mL/min). The flow rates of the pure gases were monitored by mass flow controllers and the gas stream at the outlet of the column was analyzed with a mass spectrometer. The breakthrough curves are represented in the form of the normalized gas ion intensities  $I_i/I_{i,0}$ , where  $I_i$  is the measured ion intensity of component  $i$  at the column outlet and  $I_{i,0}$  being the feed gas intensity of component  $i$ .



**Figure S16.** Breakthrough curves of an equimolar mixture of CO<sub>2</sub> and CH<sub>4</sub> at 298 K over UiO-66-X compounds.

**Table S1.** The first weight loss in TG curves for the different forms of the UiO-66-X compounds and its assignment.

Compound	Number of Guest Molecules Removed Below Decomposition Temperature	Weight Loss (%): Obs. / Cal.
<b>1-AS</b>	1.5 (H <sub>2</sub> BDC-SO <sub>3</sub> H)	14.7 / 14.7
<b>2-AS</b>	2.0 (H <sub>2</sub> BDC-CO <sub>2</sub> H)	17.4 / 17.9
<b>3-AS</b>	2.0 (H <sub>2</sub> BDC-I)	19.5 / 19.4
UiO-66-AS	3.0 (H <sub>2</sub> BDC)	23.2 / 23.0
<b>1</b>	7 (H <sub>2</sub> O)	5.6 / 5.5
<b>2</b>	22 (H <sub>2</sub> O)	17.0 / 17.0
<b>3</b>	4 (H <sub>2</sub> O)	3.0 / 2.9
UiO-66	11 (H <sub>2</sub> O)	10.4 / 10.6

**Table S2.** Frequencies of DRIFT bands<sup>[a]</sup> for the empty-pore forms of UiO-66-X compounds and as-synthesized form of UiO-66 compound.

Compound	Frequencies (cm <sup>-1</sup> ) of DRIFT Bands
<b>1</b>	3415 (br), 1598 (s), 1495 (m), 1415 (vs), 1230 (s), 1177 (s), 1081 (s), 1024 (s), 829 (w), 776 (m), 670 (m)
<b>2</b>	3207 (br), 1707 (w), 1594 (s), 1491 (m), 1402 (vs), 1306 (w), 1263 (w), 1223 (w), 1167 (w), 1140 (w), 1071 (m), 1024 (w), 922 (w), 872 (w), 832 (sh), 812 (w), 776 (m), 716 (w), 670 (m)
<b>3</b>	3673 (m), 1704 (w), 1591 (vs), 1472 (s), 1392 (vs), 1280 (w), 1256 (w), 1160 (w), 1038 (m), 922 (w), 870 (w), 826 (w), 809 (sh), 766 (m), 743 (m), 713 (m), 683 (s)
UiO-66-AS	2932 (br), 1661 (s), 1558 (s), 1508 (m), 1395 (vs), 1300 (w), 1259 (w), 1156 (w), 1095 (w), 1020 (w), 887 (w), 822 (w), 801 (sh), 747 (s), 709 (sh), 665 (s)
UiO-66	3680 (m), 1710 (m), 1588 (vs), 1508 (s), 1425 (sh), 1405 (vs), 1322 (w), 1256 (w), 1223 (w), 1160 (m), 1104 (w), 1018 (m), 902 (s), 885 (w), 816 (m), 746 (sh), 730 (s), 706 (sh), 687 (s)

<sup>[a]</sup> Abbreviations: s = strong; vs = very strong; m = medium, w = weak, sh = shoulder.

**Table S3.** Selected frequencies ( $\text{cm}^{-1}$ ) of DRIFT bands for the different forms of UiO-66-X compounds and their assignments.

Compound	Asymmetric Stretching of $-\text{CO}_2$ Group	Symmetric Stretching of $-\text{CO}_2$ Group	Stretching of $-\text{CO}_2\text{H}$ Group	Stretching of $-\text{OH}$ Group
<b>1-AS</b>	1596	1412	1658	-
<b>1</b>	1597	1412	-	-
<b>2-AS</b>	1596	1398	1716, 1658	-
<b>2</b>	1594	1405	1710	-
<b>3-AS</b>	1596	1395	1658	-
<b>3</b>	1588	1392	1700	3673
UiO-66-AS	1586	1395	1665	-
UiO-66	1588	1405	1710	3680