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Electronic Supplementary Information (ESI)

Environmentally benign dry-gel conversions of Zr-based UiO metal-organic frameworks with high yield and possibility of solvent re-use

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Section S1. Structure of UiO-66

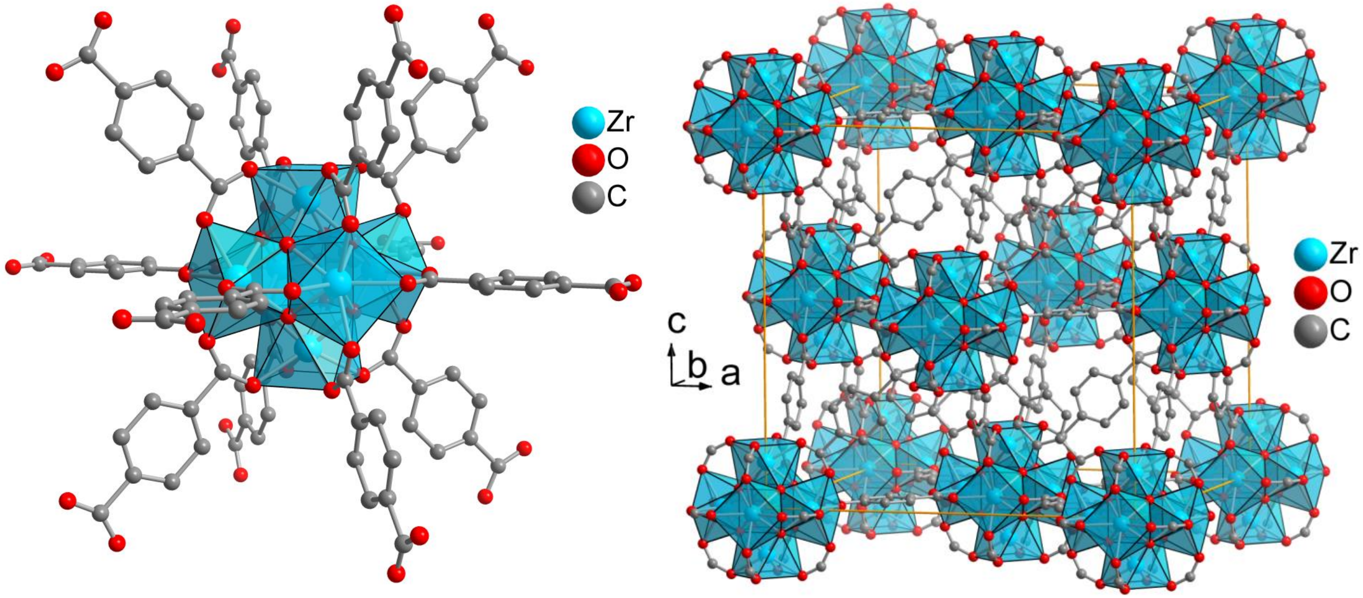

Figure S1 Crystal structure of zirconium terephthalate UiO-66.[1] The SBU is an octahedral cluster of six vertex-sharing ZrO_8 square-antiprism, which is connected to 12 neighboring SBUs in a face-centered cubic (fcc) packing arrangement. The Zr-MOF structures formed with linear ligands are therefore expanded versions of the cubic close packed (ccp) structure (= fcc). The Zr-MOF structures can be extended with increasing length of the linker from phenyl (in BDC with UiO-66) over biphenyl (in BPDC with UiO-67) to terphenyl (UiO-68) with retention of the framework topology (isoreticular structures). The UiO-66 structure is drawn from the deposited cif-files under CCDC 837796.[2]

Section S2. Determination of defects from thermogravimetric analysis (TGA)

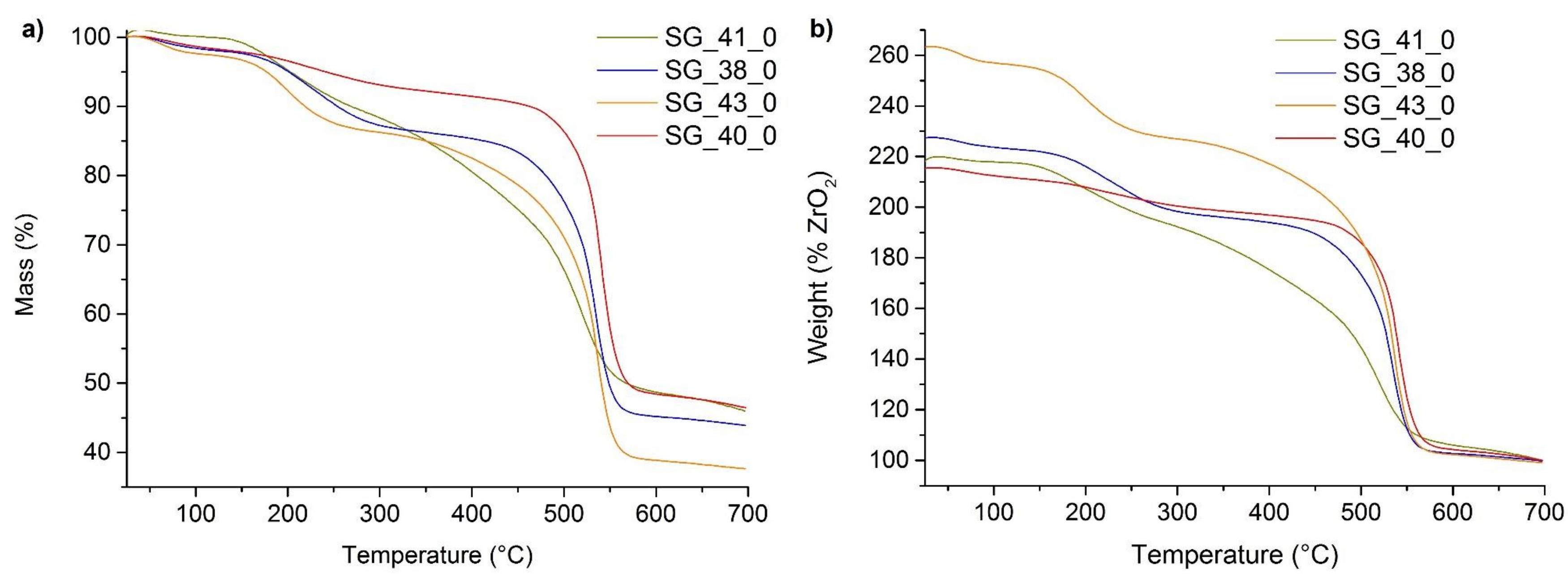

Figure S2 TGA of selected UiO-66 and UiO-67 materials: a) normalized such that the initial weight = 100% and b) normalized such that the final weight = 100%. The legend SG_xx_x refers to the experiment numbers in Table S1-S3.

Determination of defects per SBU was carried out similar to Shearer *et. al.*.[3] Evaluation of TGA data is made with an assumption: the residue in each TGA experiment is **ZrO_2**. The reaction for decomposition of ideal (defect-free), **dehydroxylated** UiO-66 (**$Zr_6O_6(BDC)_6$**) can be described as followed:

$$Zr_6O_6(BDC)_6 \;+\; 45\,O_2 \xrightarrow{\hspace{3cm}} 6\,ZrO_2 \;+\; 48\,CO_2 \;+\; 12\,H_2O$$

First we have to determine theoretical TGA plateau weight $W_{Theo.Plat}$:

$$\mathbf{W_{Theo.Plat} = (M_{Comp}/M_{6xZrO2})*W_{End}}$$

Where:

M_{Comp} is the molar mass of dehydroxylated, defect-free composition of interest:

M_W(UiO-66) = 1628,03 g/mol
M_W(UiO-66-NH_2) = 1724,04 g/mol
M_W(UiO-67) = 2084,57 g/mol
M_{6xZrO2} is the molar mass of 6 moles of zirconium oxide (**739.34** g/mol)
W_{End} is the end weight of the TGA run (= **100 %** if normalized as described above).

$W_{Theo.Plat}$ for dehydroxylated UiOs:
$W_{Theo.Plat}$ (UiO-66) = 220.20 %
$W_{Theo.Plat}$ (UiO-66-NH_2) = 233.19 %
$W_{Theo.Plat}$ (UiO-67) = 281.95 %

The weight contribution per BDC linker **$Wt.PL_{Theo}$** can be determined by following equation:

Where: **NL_{Ideal}** is the number of linkers (6) in the ***ideal*** Zr_6 formula unit

$Wt.PL_{Theo}$ = (**$W_{Theo.Plat}$ − W_{End}**)/**NL_{Ideal}**
$Wt.PL_{Theo}$ (UiO-66) = (220.20−100)/6 = 20.03 %
$Wt.PL_{Theo}$ (UiO-66-NH_2) = (233.19 −100)/6 = 22.20 %
$Wt.PL_{Theo}$ (UiO-67) = (281.95 −100)/6 = 30.33 %

The experimental number of linkers per ***defective*** Zr_6-SBU, **NL_{Exp}** can be determined by following equation:

NL_{Exp} =(6-x)=($W_{Exp.Plat}$ − W_{End})/ $Wt.PL_{Theo}$

Where:
$W_{Exp.Plat}$ is the experimental TGA plateau and can be taken from Figure S2

x is the number of linker deficiencies per Zr_6 formula unit and can be determined by following equation:

x= 6 − NL_{Exp} = 6-(($W_{Exp.Plat}$ − W_{End})/$Wt.PL_{Theo}$)

x (UiO-66-HCl/SG_38_0) = 6−4.443 = 6−((**189**−100 %)/20.03 %) = **1.557**
x (UiO-66-BA/SG_40_0) = 6−4.643 = 6−((**193**−100 %)/20.03 %) = **1.357**
x (UiO-66-NH_2-BA/SG_41_0) = 6−4.414 = 6−((**198**−100 %)/22.20 %) = **1.586**

x (UiO-67-HCl/SG_43_0) = 6−4.121 = 6−((**225**−100 %)/30.33 %) = **1.879**

With x we obtain the experimental molecular weight Mw by using **$Zr_6O_{6+x}(BDC)_{6-x}$**
SG_38_0: x = 1.6 $Zr_6O_{7.6}(BDC)_{4.4}$
SG_40_0: x = 1.4 $Zr_6O_{7.4}(BDC)_{4.6}$
SG_41_0: x = 1.6 $Zr_6O_{7.6}(BDC\text{-}NH_2)_{4.4}$
SG_43_0: x = 1.9 $Zr_6O_{7.9}(BPDC)_{4.1}$

Experimental Mw:
Mw (UiO-66-HCl) =1397.48
Mw (UiO-66-BA) = 1427.10
Mw (UiO-66-NH_2-BA) = 1463.81
Mw (UiO-67-HCl) = 1663.39

Section S3. Synthesis of UiO-67, UiO-66-NH_2 and UiO-66 through DGC method

Preparation of DGC samples:

1. A small amount (typically 2.5 mL) of DMF solvent was placed at the bottom of a 15 mL Teflon container and the modulator was added (Fig. S2a).
   In case of benzoic acid 1.4 g of modulator was dissolved.
   In case of HCl 0.5 mL of 37% aqueous HCl was used.
2. The solid starting materials were mixed and ground (Fig. S2b) ($ZrCl_4$, linker and optional benzoic acid) and placed in the DGC head (Fig. S2c).
   In case of benzoic acid 0.2 g of modulator was used.
3. DGC sieve was placed above the solvent (Fig. S2d) and covered.
4. The Teflon container was capped in a stainless steel autoclave and the heating program was started (3 h ramp to heat up, 24 h at constant temperature, 3 h ramp for cooling down).
5. The as-synthesized product was obtained (Fig. S2e) and washed with DMF (2 x 5 mL) and ethanol (5 mL).

The preparation of the DGC samples and the used Teflon objects (sieve, rings and container) including their sizes are shown in Figure S3.

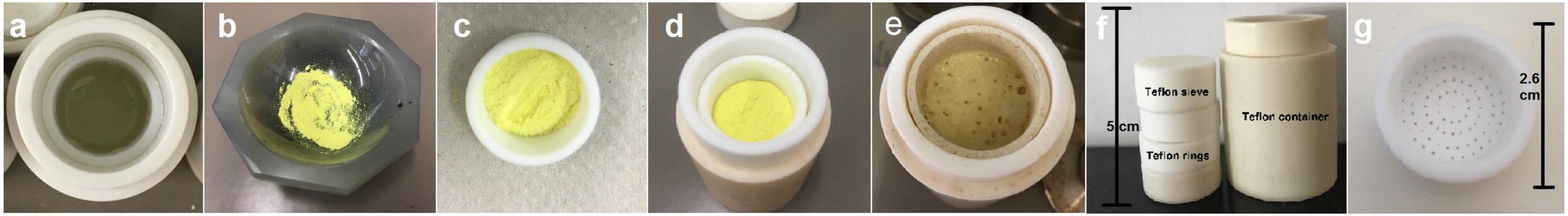

Figure S3 Pictures of sample preparation (a-e) and used Teflon objects for DGC (f and g).

Table S1 Dry gel conversion synthesis of UiO-67-HCl.

Experiment	$ZrCl_4$ [mmol]	H_2BPDC [mmol]	DMF [mL]	HCl [mL]	Conditions (Time, Temp.)	Washing procedure (DMF, EtOH)	BET surface area [m²/g]	Yield [mg]
SG_43_0	0.26	0.26	2.5	0.5	24 h, 150 °C	DMF (x2)	2369	82

Table S2 Dry gel conversion of UiO-66-NH_2-benzoic acid.

Experiment	$ZrCl_4$ [mmol]	NH_2-H_2BDC [mmol]	DMF [mL]	Benzoic acid [mmol]	Conditions (Time, Temp.)	Washing procedure (DMF, EtOH)	BET surface area [m²/g]	Yield [mg]
SG_29_0	0.26	0.26	5.0	13*	24 h, 120 °C	DMF (x2), EtOH (1x)	505	80
SG_33_0	0.26	0.26	3.5	13*	24 h, 120 °C	DMF (x2), EtOH (1x)	672	74
SG_30_2	0.26	0.26	2.5	13*	24 h, 120 °C	DMF (x2), EtOH (1x)	726	52
SG_30_3	0.26	0.26	2.5	13**	24 h, 120 °C	DMF (x2), EtOH (x1)	780	30
SG_36_0	0.26	0.26	2.5	13***	18 h, 120 °C	DMF (x2), EtOH (x1)	935	80
SG_41_0	0.26	0.26	2.5	13***	24 h, 120 °C	DMF (x2), EtOH (x1)	1023	93

*benzoic acid only at the bottom of the container in the DMF solvent, **benzoic acid only in DGC head, ***benzoic acid at the bottom of the container in the DMF solvent and in the DGC head,

Table S3 Dry gel conversion of UiO-66-benzoic acid and UiO-66-HCl.

Experiment	$ZrCl_4$ [mmol]	H_2BDC [mmol]	DMF [mL]	Benzoic acid [mmol]/ HCl [mL]	Conditions (Time, Temp.)	Washing procedure (DMF, EtOH)	BET surface area [m²/g]	Yield [mg]
SG_35_0	0.26	0.26	2.5	BA: 13***	18 h, 120 °C	DMF (x2), EtOH (1x)	860	40
SG_40_0	0.26	0.26	2.5	BA: 13***	24 h, 120 °C	DMF (x2), EtOH (1x)	1242	83
SG_38_0	0.26	0.26	2.5	HCl: 0.5	24 h, 120 °C	DMF (x2), EtOH (1x)	1461	65

***benzoic acid at the bottom of the container in the DMF solvent and in the DGC head

As an explanation for the effect of BA in the solvent we refer to the vapor pressure of BA of 5.8 hPa at 117 °C.[4]

In the following images we illustrate the influence of BA addition to solvent at the bottom of the Teflon container. If we do not use a solvent-modulator mixture (see a) and b)) a large part if not all of the MOF product is washed into the solvent (see c)). Hence, the solvent cannot be re-used. In case of a solvent-BA mixture the MOF will not be washed from the sieve (see a) and b)). We suggest that the amount of BA present in the solvent vapor will reduce the solubility of BA from the DGC head. Further, the BA-saturated DMF vapor may supply fresh BA which then also leads to a thicker and more stable dry gel.

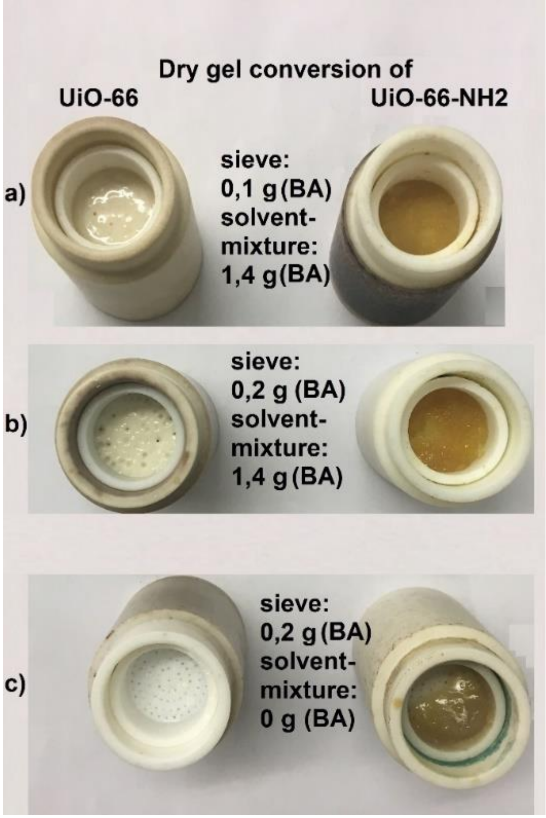

Figure S4 Influence of BA in solvent: a) and b) DMF/BA solvent-mixture c) only DMF.

Section S4. Comparison of UiO-66 through DGC and solution synthesis

Standard solvothermal synthesis of UiO-66

A standard solvothermal synthesis of benzoic acid modulated UiO-66 is performed by dissolving $ZrCl_4$ (60 mg, 0.26 mmol), BDC (44 mg, 0.26 mmol) and benzoic acid (1.6 g, 13.13 mmol) at room temperature in 15 mL of DMF. This solution was capped and sealed in a vial, and allowed to react solvothermally at 120 °C for 24 h. After cooling, the mixture was centrifuged, then the solids were left to soak in MeOH for 3 d. The solution was exchanged with fresh MeOH (37.5 mL) every 24 h. After 3 d of soaking, the solids were centrifuged and dried under vacuum.[5] The solution synthesis delivered a reproducible yield of 80 mg.

Table S4 Comparison of UiO-66 through DGC and solution synthesis; Table taken from literature 10 and supplemented by results of DGC method.

Items	UiO-66[1]	UiO-66[6]	UiO-66[7]	UiO-66[8]	UiO-66[9]	**UiO-66-HCl-DGC/ SG_38_0**	**UiO-66-BA-DGC/ SG_40_0**
$ZrCl_4$ (mg/mmol)	53/0.227	80/0.343	125/0.540	51300/220	116/0.500	**60/0.26**	**60/0.26**
H_2BDC (mg/mmol)	37/0.227	57/0.343	123/0.75	35600/220	83/0.5	**44/0.26**	**44/0.26**
Modulators (mL/g)	N.A.	Acetic acid 0.5	HCl 1.0	Formic acid 0.83	Formic acid 1.89	**HCl 0.5**	**Benzoic acid 1.6**
DMF (mL)*	26	20	15	2000	18	**2.5**	**2.5**
Modulator/ligand molar ratio	N.A	30	15.5	100	100	**22.4**	**50**
Temperature (K)	393	393	353	393	393	**393**	**393**
Time (h)	24	24	12	24	24	**24**	**24**
Product types	Cubic (~100nm)	Octahedral (~200nm)	Spherical (~200nm)	Octahedral (~3µm)	Octahedral (~300nm)	**Octahedral (~150nm)**	**Spherical (~250nm)**
BET/ Langmuir surface area (m²/g)	N.A./1187	1400/N.A.	1580/N.A.	1367/N.A.	1730/2047	**1461/N.A.**	**1242/N.A.**

*used amount of DMF during synthesis (washing not included)

Section S5. Powder X-ray diffraction of UiO-66 and -67 materials

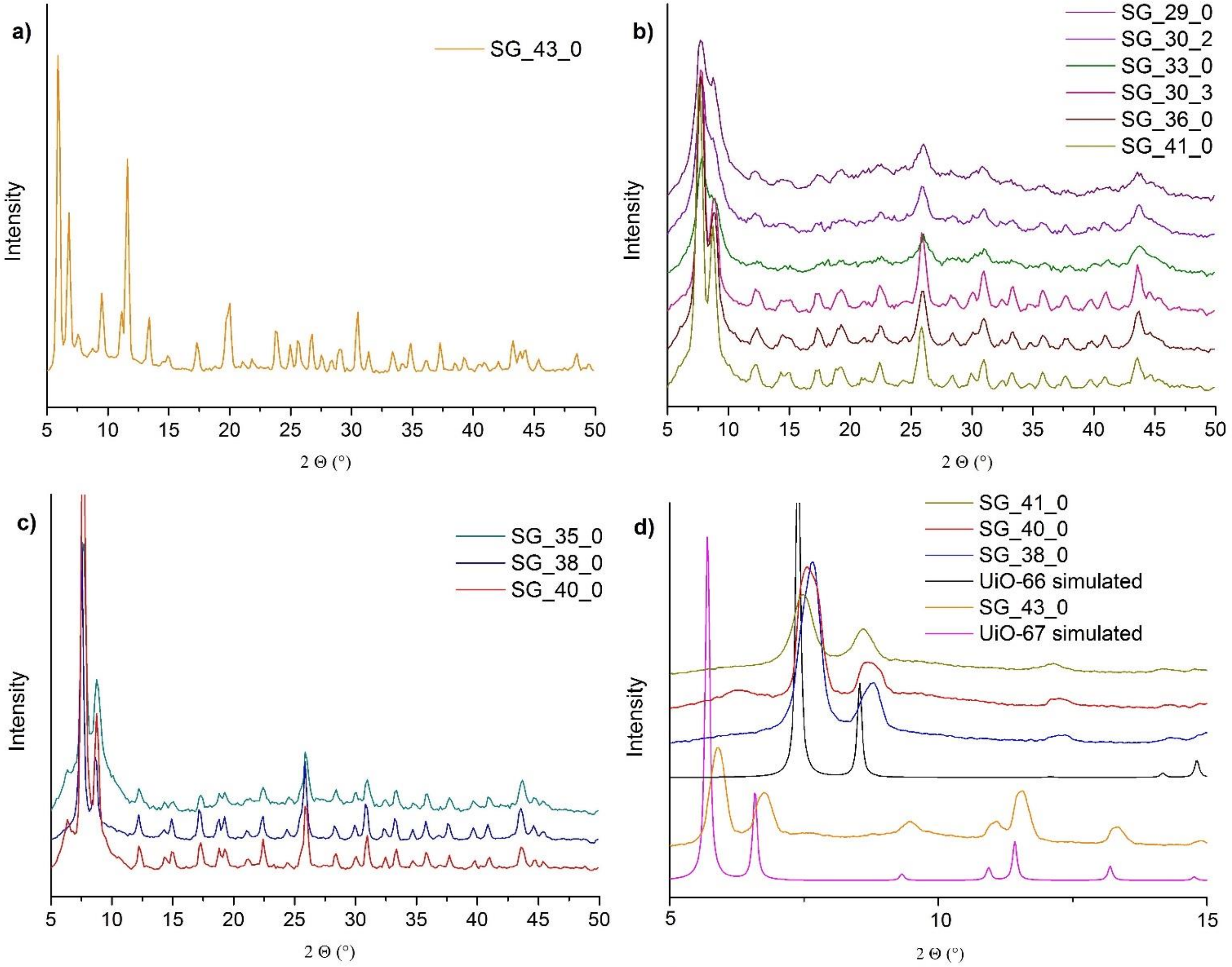

Figure S5 PXRD patterns of DGC products (a) UiO-67-HCl, (b) UiO-66-NH_2-benzoic acid, (c) UiO-66-BA or UiO-66-HCl materials and (d) enlarged low angle (2θ = 5-15°) region of Fig. 2 in the manuscript. The legend SG_xx_x refers to the experiment numbers in Table S1-S3.

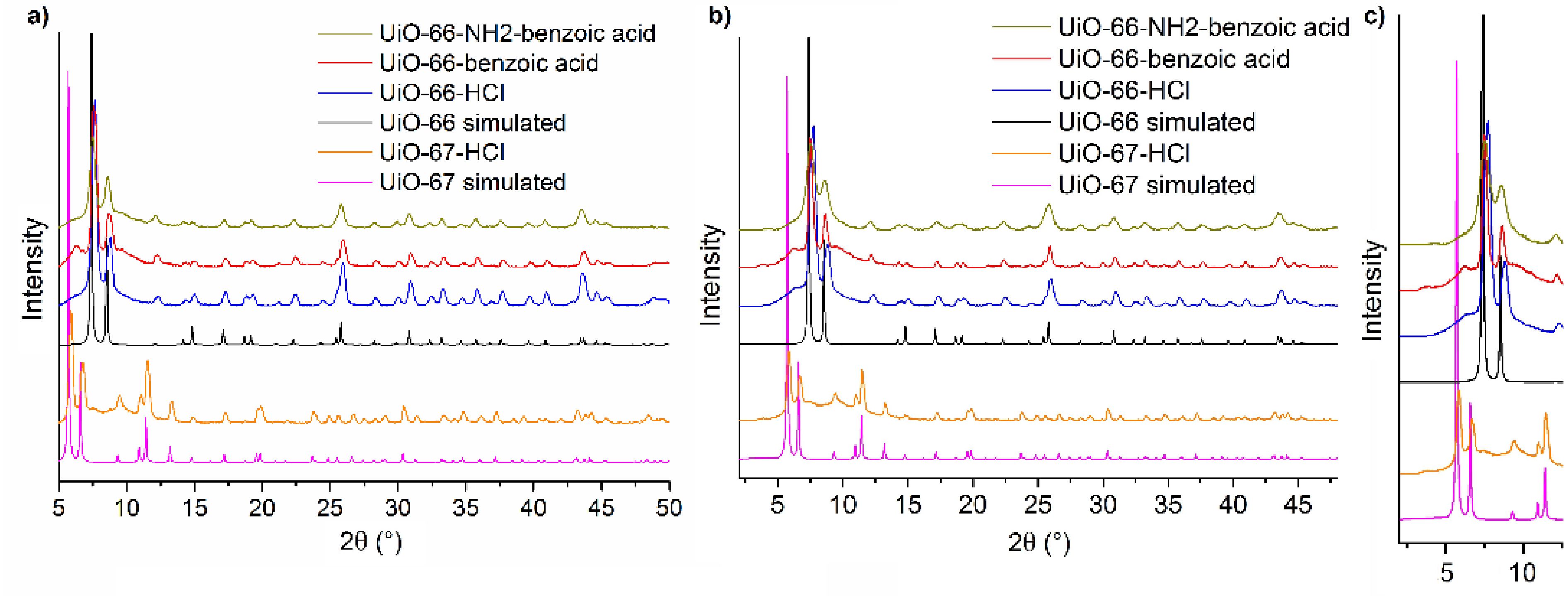

Figure S6 (a) PXRD-pattern in a 2θ range of ca. 5–50° (repeated from manuscript Fig. 2); (b) PXRD-pattern in a 2θ range of ca. 2–48°; (c) enlarged low angle of (b) in the range 2θ = 2-12.5°.

Section S6. Pore size distribution and elemental analysis of selected UiO-66 and -67 materials

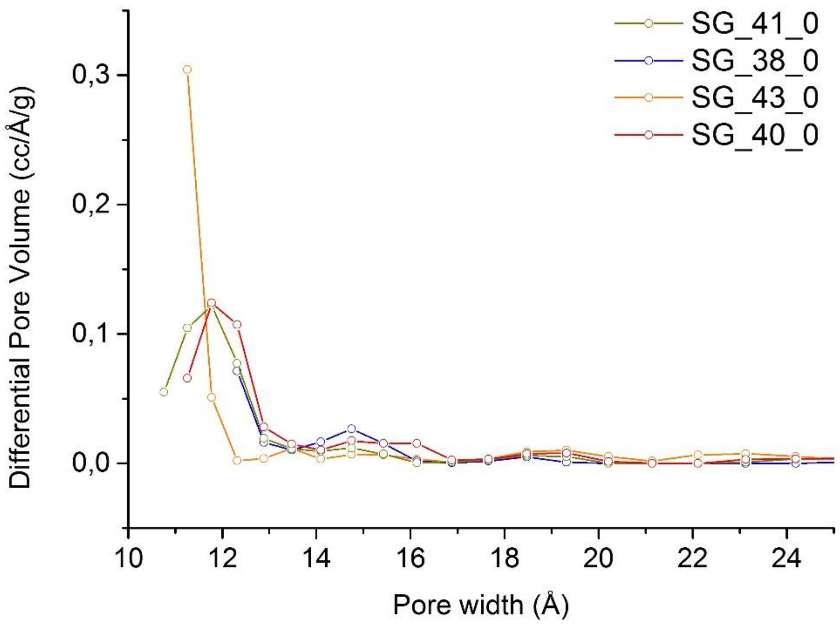

Figure S7 Pore size distribution of selected UiO-66 and UiO-67 materials. The legend SG_xx_x refers to the experiment numbers in Table S1-S3.

Table S5 CHN-Analysis of selected UiO-66 and UiO-67 materials. The legend SG_xx_x refers to the experiment numbers in Table S1-S3.

CHN analyses were performed with a Perkin Elmer CHN 2400 series 2 elemental analyzer.

MOF	%C	%H	%N
UiO-66			
SG_38_0	32.22	3.61	/
SG_40_0	32.32	3.73	/
ideal UiO-66 $Zr_6O_4(OH)_4(BDC)_6$	theor. 34.61	theor. 1.68	theor. /
$Zr_6O_{7.6}(BDC)_{4.4}$	30.23		
$Zr_6O_{7.4}(BDC)_{4.6}$	30.94		
UiO-66-NH₂			
SG_41_0	31.76	3.72	5.01
ideal UiO-66-NH_2 $Zr_6O_4(OH)_4(NH_2\text{-}BDC)_6$	theor. 32.76	theor. 2.28	theor. 4.78
$Zr_6O_{7.6}(NH_2\text{-}BDC)_{4.4}$	28.86		
UiO-67			
SG_43_0	42.38	3.78	/
ideal UiO-67 $Zr_6O_4(OH)_4(BPDC)_6$	theor. 47.54	theor. 2.45	theor. /
$Zr_6O_{7.9}(BPDC)_{4.1}$	41.41		

The results of the elemental CH(N)-analysis are qualitatively in line with the found defects from thermogravimetic analysis in Section S2. The decrease of the % C compared to the theoretical value for the ideal UiO structure is dues to the presence defects, that is, missing linkers in relation to the Zr_6 SBU. The increase of %H and the higher %C can be explained with small residues of DMF (%C 49.30, %H 9.65) and adsorbed water/moisture from air through the UiO hydrophilicity and capillary effects upon sample handling under air. In view of the difficult to assess solvent content in MOFs we refrain from further detailed analysis of the CH(N) data.

Section S7. Scanning electron microscopy (SEM) images of selected UiO-66 and -67 materials

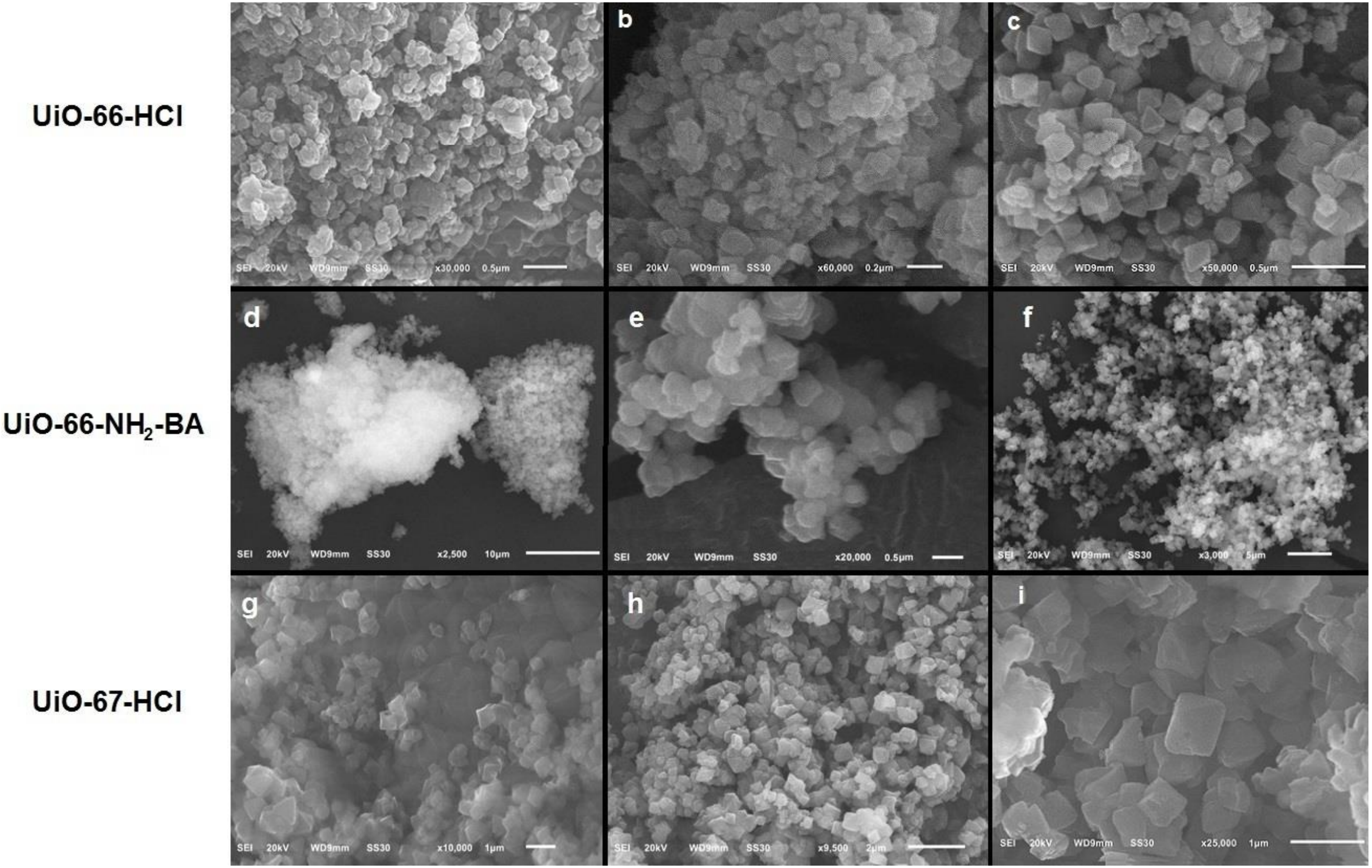

Figure S8 Scanning electron microscopy images of selected UiO-66 and -67 materials.

Section S8. Reproducibility of DGC for UiO-66-BA without re-use of solvent

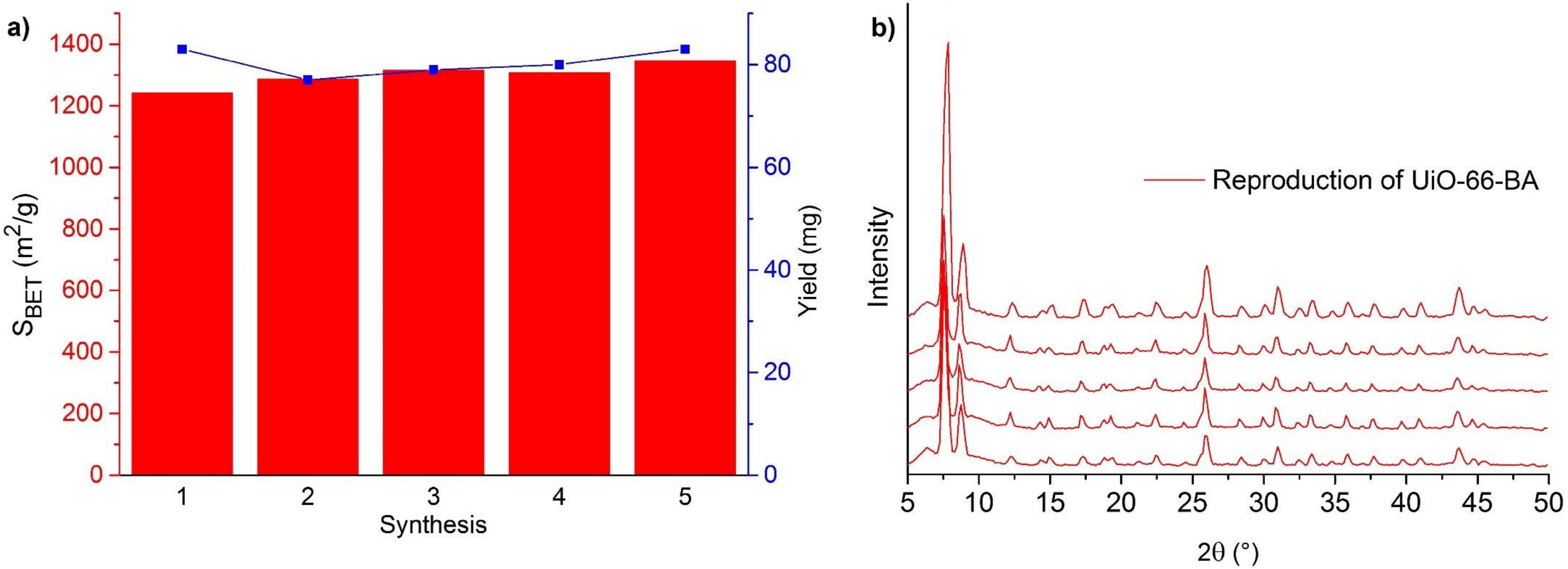

Figure S9 Reproducibility of UiO-66-BA without re-use of solvent. a) Surface area and yield; b) PXRDs of the product from each synthesis 1-5 (synthesis 1 at bottom).

Section S9. Results of five synthesis runs with solvent re-use for UiO-66-NH_2

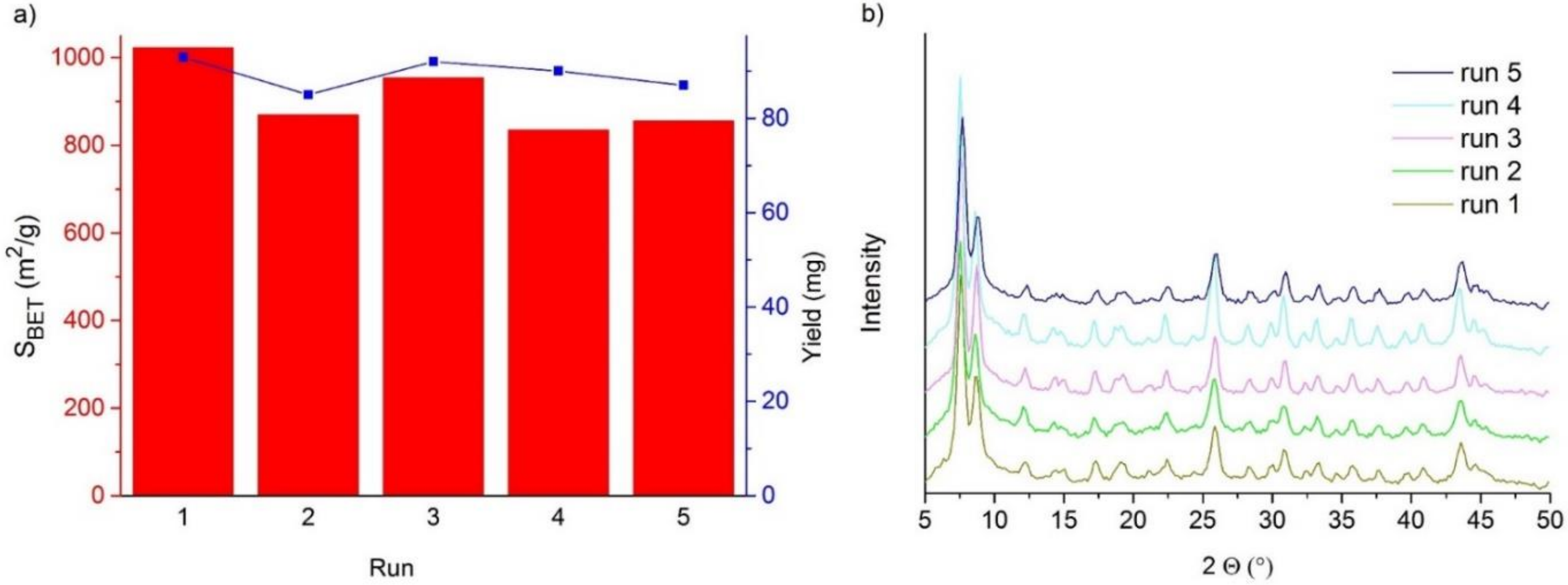

Figure S10 Results of five DGC runs re-using the same solvent/modulator mixture for UiO-66-NH_2-BA. a) Surface area and yield of UiO-66-NH_2-BA and b) PXRDs of each run.

Section S10. References

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